ASSESSING THE FATE OF CRUDE OIL IN ARCTIC COASTLINE SEDIMENTS:

EFFECT OF EXPOSURE TIME AND SEDIMENT STRUCTURE

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A

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Abstract

The research presented in this thesis will allow for a better understanding of how crude oil interacts with the shoreline. Offshore oil production along Alaska's arctic coast is expected to increase in coming years. While this is likely to create large economic benefits for the state, crude oil spills may occur. An oil spill may reach the shoreline, where it could create adverse short and long-term ecological effects. Mass transfer processes, affected by sediment characteristics, play an important role in determining the fate of crude oil along shorelines. Crude oil viscosity and diffusion are strongly temperature dependent. Nutrients, commonly added to stimulate bioremediation, may be washed out with waves and tides. It is therefore necessary to study how factors such as the beach matrix, nutrient addition and temperature affect hydrocarbon distribution. Laboratory experiments were implemented to help better understand how the soil composition and tidal action will affect the oil's movement through the shoreline sediments. Experiments were conducted for two different sediment types (sandy-gravel versus pebble) obtained from Barrow, AK and two different temperatures (20° and 3° Celsius). A microcosm study using a PVC pipe set-up was used to simulate the transport of oil through the sediment profile. Data obtained from this study show that the amount of pooling and its location was dependent on sediment structure. In sandy gravel sediment, Total petroleum hydrocarbons (TPH) persisted 6 inches below the surface, indicating pooling does occur. In pebble sediment, TPH persisted at the top and bottom of the column, but only for the first few days, indicating the pooling would not be a long term problem. Both sediments had higher CO_2 production at higher temperatures, with the highest respiration, i.e. more biodegradation, found in sandy-gravel. While CO_2 releases were slightly higher in sediments with the addition of fertilizer, overall the application of fertilizer did not have a significant impact on the fate of crude oil in shoreline sediments.

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Chapter 1 Introduction

1.1 Background

The expected increase in offshore oil production in Alaska, combined with potential opening of the Northwest Passage in the coming years, could lead to an increase in barge and tanker traffic through the Arctic. It has been projected that hundreds of tankers will soon travel through the Passage in summer months (Smith and Stephenson 2013). This drastically increases the chance of a spill as tankers are not as thoroughly regulated as companies drilling on Alaska's North Slope. Tankers that are not equipped to handle the Arctic conditions could present a high risk to cause an accidental release. There is not only a chance for a crude oil spill, but also for a bunker oil spill. Figure 1 below shows the estimated shipping route for ships with icebreaking capability (red) and ships designed for ice-free waters (blue).

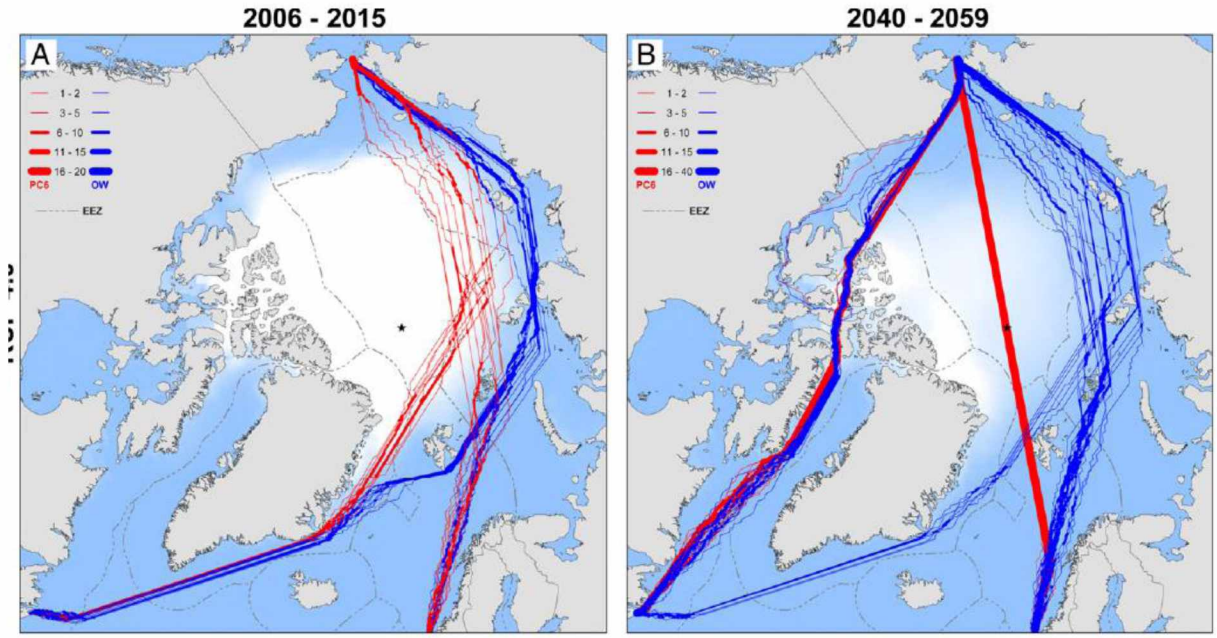

Figure 1: Estimated shipping routes (Smith and Stephenson 2013).

Open ocean petroleum spills will have different effects on the associated biota depending on the size of the spill and therefore will require different response tactics. Small scale petroleum spills that occur in the ocean can be readily degraded. Smaller spills can therefore generally be left to undergo natural attenuation and biodegradation.

Large scale spills introduce oil at a high rate which can overwhelm some of the marine organisms capable of removing hydrocarbons from the system. Fauna in the environment likewise can become engulfed in the spill and die off. Microscopic organisms such as zooplankton and phytoplankton are important bottom species in the food chain; this is especially true in the Arctic where many species ranging from small fish to whales rely on these organisms for food. A loss or reduction of these key microscopic organisms could have detrimental effects on the entire ecosystem.

Several studies have investigated clean-up methods and crude oil biodegradation in the context of an open ocean spill (Jernelöv, 2010). The Arctic Ocean is nearly surrounded by land on all sides. If an open ocean spill were to occur, it is highly likely the oil will reach the shoreline. While studies have been done in tropical regions for shoreline oil spills, there has not been a complete study on how the Arctic shoreline, with greatly different temperatures and varied sediment structure, will respond.

Accidental releases of petroleum can occur and mitigation needs to be planned. In the near future Alaska could see both the opening of the Beaufort Sea for drilling and the Northwest Passage for shipping. The knowledge of crude oil movement and its fate when it reaches the shoreline is extremely important. A large petroleum release is unavoidable as both shipping and drilling continue to rise (Smith and Stephenson, 2013). If a spill occurs and reaches land, both terrestrial

and marine life can be impacted. This impact can carry into this new ecosystems and can affect a large number of organisms both macro and microscopic.

1.2 Purpose

The research presented in this thesis will allow for a better understanding of how crude oil interacts with the shoreline sediment. Mass transfer processes play an important role in determining the fate of crude oil along shorelines. Crude oil viscosity and diffusion are strongly temperature dependent. Nutrients added to stimulate bioremediation may be washed out with waves and tides. It is therefore necessary to study how factors such as the beach matrix and temperature affect hydrocarbon and nutrient distribution. Identifying the location where oil will pool is essential in helping future research focus on microbial degradation of hydrocarbons in the respective conditions. Furthermore, knowing the depth to which crude oil penetrates the sediment, along with the ability to predict how an environment will react to a spill under specific environmental conditions, will help to create a better environmental response plan.

This study recreated in a laboratory setting a natural shore environment, simulating conditions of the Chukchi and Beaufort Sea shores. In Barrow, Alaska, two different sediment types were encountered and samples were collected. Sandy gravel sediment was found on the east side of Point Barrow, while pebble sediment was found west of Point Barrow. Experiments were conducted by introducing crude oil to both types of sediment (sandy-gravel and pebble). The effectiveness of fertilizer addition (both solid and liquid) was examined to determine if nutrient addition had a significant impact on CO_2 production. In Arctic regions temperature can vary extremely depending on the season; the average summer temperature in Barrow is near 3°C. In order to compare the collected data with temperate climate zones, the studies were done at two different temperatures (3°C and 20°C), to determine if temperature has a significant effect on oil

movement and degradation. Through a variety of analyses, the actual fate and movement of the crude oil was determined for the two different sediment types. The crude oil's fate was determined by tracking its movement through the sediment profile (top, middle, and bottom) via soil sampling, and determining whether it was released back into the environment through wash out, converted to CO_2 or volatilized.

1.3 Hypotheses

- Crude oil concentrations will be lower in pebble versus sand-gravel sediment
- Oil pooling should be visible in sandy-gravel, but not pebble sediments
- Lower temperatures should inhibit crude oil movement, therefore causing higher TPH concentrations especially in the upper layers.
- Higher temperatures will allow for higher CO_2 production
- Addition of fertilizer should have a positive influence on CO_2 production
- Solid fertilizer should have greater impact on CO_2 production than liquid fertilizer.

Chapter 2 Literature Review

2.1 Oil in the Arctic

Alaska's oil industry has grown tremendously following the discovery of oil in Prudhoe Bay and the subsequent construction of the Trans-Alaska Pipeline. Alaska contains two areas that act as petroleum reserves, the National Petroleum Reserve-Alaska (NPRA) and the Arctic National Wildlife Refuge (ANWR). It is not yet clear if these areas will be opened to petroleum drilling, but steps are currently in progress that could have drilling occur in the next few years. If both areas are opened for drilling, the land-based oil production in Alaska could dramatically increase (Schratzberger et al. 2003). Many companies are currently working on obtaining the drilling rights and permits to drill offshore. This portends that the transportation of oil over land and sea may increase in the coming years (Deppe et al. 2005). The combined effects of oil companies increasing the amount of rigs located on the North Slope and the opening of the Northwest Passage within the next 5 years greatly increases the probability of an oil spill occurring.

The increase in drilling activity in the Arctic makes Alaska susceptible to oil spills (Mohn et al. 2001). A very limited road system, seasonal changes, and a lack of infrastructure make drilling and the subsequent remediation after a spill a difficult task (McCarthy et al. 2004). For the majority of the year large areas of the Arctic Ocean are ice-covered, restricting ship traffic and thereby potentially resulting in delayed action from response crews. Unlike the Deep Water Horizon and Exxon Valdez spills, there is not a close network of crews and ships that can assist quickly. Booms, skimmers and other removal devices would take time to set-up, allowing the oil to travel greater distances and potentially reach land.

2.2 Oil Types

Each fuel type and its components can create a different response in the environment. Refined products such as diesel and gasoline contain shorter carbon chains, which allows for easier degradation and breakdown (Atlas et al., 1981). With the increase in shipping and drilling, there is an increased risk for a spill of either a crude oil or bunker fuel. These contain large quantities of more persistent long chain hydrocarbons that are not easily volatilized or degraded, thus posing a greater challenge than spills of other types of fuels.

2.2.1 Crude Oil

Crude oil is a complex mixture of hydrocarbons (Thomassin-Lacroix et al. 2002). The mixture contains molecules that have a wide range in the number of carbons present (C_1-C_{36}); the majority of petroleum products are based on hydrocarbon chains between 5 and 18 carbon atoms (C_5-C_{18}) (Chang et al. 2011). Petroleum products used today are created by refining crude oil by processing and separating the oil into different hydrocarbon groups. Refined hydrocarbons can then be used to create new products ranging from gasoline to asphalt. Generally the oil constituents can be divided into three main groups: Gasoline Range Organics (GRO) which corresponds to alkanes that fall in the C_6 to C_{10} range, Diesel Range Organics (DRO) that range from C_{10} to C_{25}, and lastly Residual Range Organics (RRO) which range from C_{25} to C_{36} (DEC, 101/102/103). Both for crude oil in its natural form or after processing and refining "the qualitative hydrocarbon content of the petroleum mixture influences the degradability of individual hydrocarbon components" (Atlas et al., 1981). The large diversity of the individual components found in petroleum makes each mixture of petroleum degrade at different rates, thus making evaluation of the biodegradation of hydrocarbons (remediation) more complex.

Knowing the chemical composition of petroleum, the relative rate at which it will degrade can be determined. Under normal aerobic conditions short straight chained carbon molecules such as alkanes (C_{10} or smaller) can be easily volatilized or degraded by microbes, whereas ringed-structured molecules, such as cycloalkanes (C_{10} and higher) and PAH such as naphthalene, are resistant to microbial degradation (Atlas et al., 1981). The difference in the two groups is based on the structure of the compound. Straight chained compounds undergo a process called β-Oxidation; the microbes are capable of breaking n-alkanes down through carboxylation into acetyl-CoA. This can then be introduced into the Krebs cycle and be completely mineralized to CO_2 (Atlas et al., 1981). On the other hand, cyclic compounds such as naphthalene (do not confuse with naphthenes) have to go through the β-ketoadipate pathway. Using oxygen, the cyclic ring can be slowly broken down into a diol and then cleaved, thereby separating carbons from the chain. This process can be very slow compared to the degradation of straight chained hydrocarbons, which is why n-alkanes (straight chain) are more favorably degraded by microbes (Atlas et al., 1981).

2.2.2 Bunker Fuel

Bunker fuel technically refers to any type of fuel that is used in shipping, but most typically refers to fuel used to power a ship's engine. Bunker fuel is composed of higher end (heavier) hydrocarbon chains, it is considered "bottom of the barrel" as it is one of the last refined petroleum products. The heavier hydrocarbons have too high of a viscosity to be used efficiently in motor vehicles and boats. For this reason this viscous fuel is generally used as a fuel in large ships. The expected increase in the use of tankers and other large ships in the Arctic and the slow biodegradation of heavier hydrocarbons (Mazraati, 2011) are two reasons why more research needs to be conducted to understand the effects on bunker oil and its remediation in the Arctic.

2.3 Oil Spill Sources

The remoteness of the Arctic and its susceptibleness to petroleum spills makes it an important study area. Spills can range from leaking tanks to large spills that can affect the entire ecosystem. Leaking tanks, natural oil seeps and other small scale spills will not be the focus of this report but are still important scenarios for which proper spill response is needed.

Before strict regulations were enforced, tanker spills contributed significantly to the overall input of oil into the marine environment by humans. In the past 40 years the average input of oil from tankers has decreased from 314,000 tons in the 1970s, to 100 tons in 2009 (Jernelöv, 2010). As tankers become equipped with double hulls and are sectioned off, the chance of stopping a spill before it becomes catastrophic has increased immensely. As tanker spills have been decreasing at a consistent rate, there is still no apparent trend for marine blow outs. Blowouts usually occur in shallow environments (Jernelöv, 2010). Currently the proposed 6 rigs that will be placed 125 miles west of Barrow will only be in 140 feet of water (Shell, 2015). In the near future drilling off the coast of Alaska will begin; it is expected to start in 2015 or 2016. While marine blowouts are rare, they can have catastrophic effects (Jernelöv, 2010). The severity of large open water spills, which are of great concern, depends on a variety of factors such as weather, tidal range, ocean current, and composition of oil released (Spaulding, 1988).

2.4 Oil Transport in the Marine Environment

When oil spills occur, the three environmental factors that affect the movement of oil are the wind, current and wave field force (Spaulding, 1988). Once the oil contacts the water, it will start spreading; the overall extent of the spill will be influenced by the evaporation, dissolution and dispersion of the oil. Some components of crude oil are highly volatile. Volatilization can account for 20-40% of the total spilled oil being removed (Spaulding, 1988). Evaporation effectively

removes shorter hydrocarbon chain molecules (Atlas et al., 1981). However larger molecules will remain. Wind and breaking waves will disperse the oil, which allows for a greater surface available for microbes, facilitating some degradation, but the majority of the oil will remain (Spaulding, 1988) and needs to be treated with additional methods, or the spill could reach land.

2.5 Shoreline Treatment Options

Once the oil reaches the shore, a variety of different methods have been used successfully to clean-up shorelines. A common practice for oil spills on land is bioremediation, i.e. the deliberate enhancement of contaminant degradation by microbes, e.g. by adding nutrients, electron acceptors or microbes. The Exxon Valdez oil spill in Prince William Sound is "the largest and most thoroughly studied application of bioremediation in the field" (Schratzberger et al. 2003). The application of bioremediation, with addition of nutrients, helped to increase oil removal compared to control plots on shore. Remnants of the spill can still be seen today, but without remediation efforts, these effects would be much worse (Schratzberger et al. 2003).

A historical approach that has been used, and is proven effective, is incineration of contaminated soil. This method, while it is effective, is generally not a safe method to use on soil in situ due to the potential deleterious effects on the environment; it generally needs to be applied in a controlled environment (Reddy et al. 2011), therefore soil is typically shipped to a dedicated facility. Although incineration has been used on land for small oil spills, burning is more common for oil spills on the water. Burning can help to reduce the amount of oil before it spreads in the marine environment or reaches land (Reddy et al. 2011). While this method has been found effective, it can require a large effort.

Another popular method used to remove petroleum spills is to wash the soil, i.e. rinse it using flowing water or wave action to transfer the oil to the water (Eriksson et al. 2003). This method

was not completely successful in the Exxon Valdez spill, since the crude oil penetrated down to the clay layer where it started pooling. Arctic beaches in the Barrow area however, are predominantly sandy-gravel and pebble, with no clear indication of a clay layer (Hume and Schalk, 1967). So it is possible that the natural movement of water could have a significant impact on the removal of crude oil.

2.6 Sediment Characteristics

2.6.1 Sediment Particle Size

Shoreline particle size and distribution of the sediment can have a large impact on the movement of oil. Higher porosity sediments contain a larger amount of voids allowing for fluids to travel more freely through the sediment. The sand sediment has a higher porosity (0.31-0.46) than the pebble sediment (0.24-0.36) but presents a much greater resistance to fluid flow through porous media because sand grains can be more neatly packed together resulting in much smaller pore sizes (Figure 2). The ability for oil to be retained in soil is inversely related to its ability to penetrate the sediment (Harper, 1978). Figure 2 shown below is an example of a pebble and sand sediment.

Additionally, the sediment particle size can affect the number of microbes present in the soil. In sediments with large grain size (such as pebbles) there is less surface area for organic matter and moisture to be retained, making it a harsh environment for microbes to survive. Sand with smaller particles allows for greater surface area and a more hospitable environment (Lynch and Hobbie 1988). Clay particles located within these sediments help to maintain organic matter, but the constant tidal flux makes it very difficult for these particles to remain in the sediment (Lynch and Hobbie 1988).

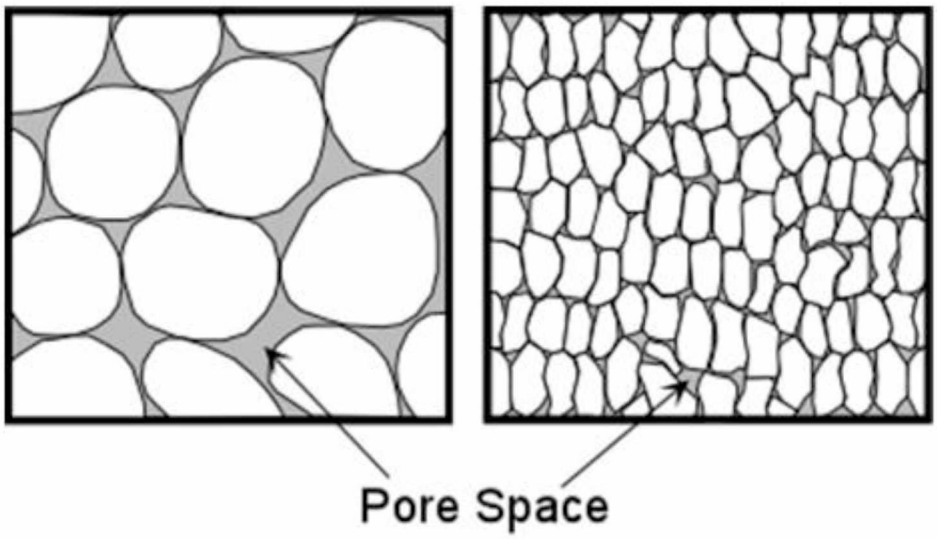

Figure 2: Difference between pebble and sand pore space (http://rmccs.org/)

2.6.2 Environmental Sensitivity Index (ESI)

Each coastal environment will respond differently to a nearby oil spill. The National Oceanic and Atmospheric Administration (NOAA) developed an Environmental Sensitivity Index (ESI) that classifies beach types and identifies the resources that are at risk. These risks include human and biological resources as well as sensitive habitats. Each ESI assemblage is grouped into different shoreline classifications. By looking at substrate type, grain size, wave action, tidal currents and river currents, a prediction of the behavior and persistence of oil in intertidal habitat can be made. If a spill were to occur, responders could then look up the affected shoreline's characteristics and determine its ESI number; which gives the responder a general idea of how oil will react in the environment, and what potential problems could arise. The ESI assigns values ranging from 1 (high levels of physical energy and low biological activity) to 10 (sheltered shorelines, high biological activity). A large part of Alaska's Beaufort and Chukchi sea shores falls under ESI 1, 4 and 5. While ESI 1 is characterized by rocky cliffs, this research will focus on ESI 4 and 5 areas

(NOAA, 2004). For ESI 4 areas with sandy material, the expected oil penetration is 10 in, ESI 5 areas with pebble sediment typically have a high oil penetration up to 20 in (NOAA, 2004).

2.6.3 Shoreline Processes

Shoreline is defined as the line where the land and the lowest point of water meet (Johnson, 1919). Therefore the low tide line is equal to the shoreline (Figure 3). Barrow, Alaska, is built on the Alaskan coastal plain, its shorelines consists of "unconsolidated recent and Pleistocene sediments" (Hume and Schalk, 1967).

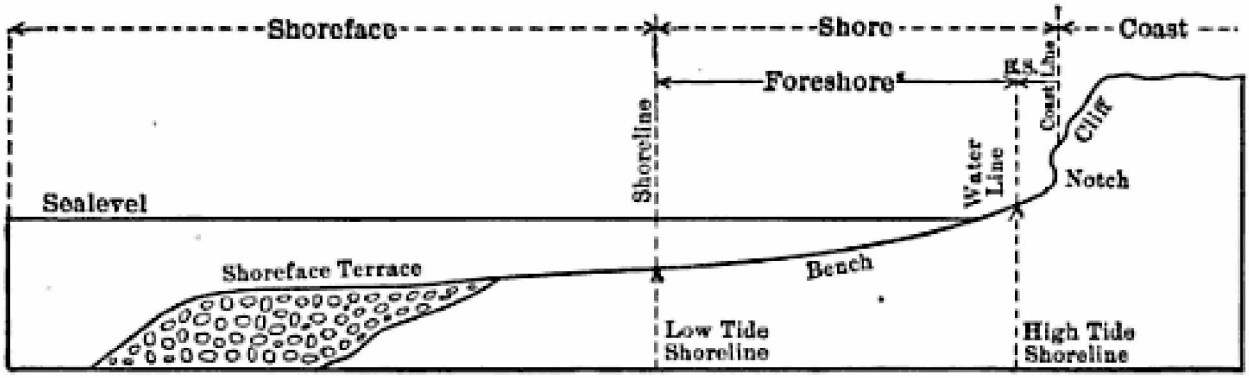

Figure 3: Shoreline development (Johnson, 1919)

Unlike most places, the tidal flux of Barrow is not significant except during a storm, with an average daily tide of roughly 6 inches (Hume and Schalk, 1967). In 2015 the maximum tidal height is expected to be 15 inches (NOAA, 2015). In the Arctic, the major factor affecting the shoreline is the build-up of ice. Ice can dampen the effects of waves thereby affecting the transport and deposition of sediments and contaminants alike (Hume and Schalk, 1967). On average the area only experiences around three months of relatively free ice conditions (Hume and Schalk, 1967).

The majority of shoreline studies only look at one single sediment type, such as sand or gravel. While these studies are easier to conduct, beaches that consist of only one sediment type are rare (Mason and Coates, 2001). The regular addition and reduction of sediments from wave action will

slowly transform a beach. Sandy-gravel sediment, such as those found in Barrow (Hume and Schalk, 1967), are mixed sediments, so they will see stronger swash and backwash on the beaches (Figure 4). Swash is the turbulent water that hits the shoreline after a breaking wave, and backwash is the turbulent water that is taken away as the ocean moves back. The stronger swash and backwash allows for the beach to have an overall better drainage. An increase in drainage means the beach could be a good candidate for natural wave action as a method of spill response (Mason and Coates, 2001).

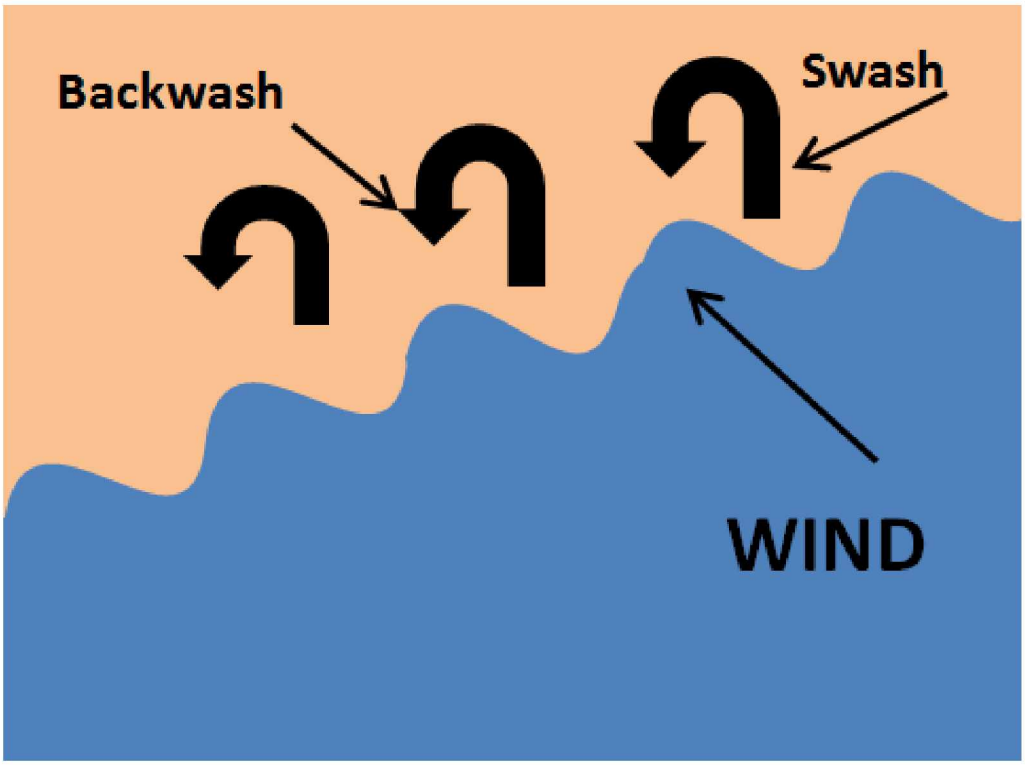

Figure 4: Diagram of swash and backwash cycle

2.7 Wave Action

The effectiveness of using waves to rinse the sediment is dependent on the energy the wave exhibits. There are two different types of waves; longitudinal and transverse. Longitudinal waves

move particles parallel to the wave and create a compressed, oscillating movement. Transverse waves will displace the particle perpendicular to the wave (Johnson, 1919). Ocean waves are a combination of both wave types; as the waves move forward it will cause particles to travel in a clockwise motion. The energy created by both wave types can be transmitted through the surface of the water body which can deliver that energy to the beach. The clockwise movement combined with the waves energy allows for the water to pull part of the shorelines sediment and its potential contaminants back into the ocean (Johnson, 1919).

Waves crash against the shoreline at a 90 degree angle and develop a longshore current, which assists in the transport of fine sediment down shore (Johnson, 1919, and Hume and Schalk, 1967). The mixed-sediment shorelines that comprise the Arctic coast and the increase in the hydraulic conductivity, swash and backwash, are positive indicators that wave action could be an effective method for shoreline clean-up in the Arctic.

2.8 Environmental Parameters

Wave action on its own, while decreasing the amount of oil present, cannot fully remove oil from the system. Bioremediation is a crucial partner in this process. Understanding the environment that a spill occurs in is crucial to understanding the fate of crude oil. As previously mentioned, varying sediment types and mixtures can have a significant impact on the movement of oil. In the Arctic climate, many other factors can influence the fate and transport of crude oil, with temperature fluctuation being a major factor. Certain practices have been adapted to try and elevate these effects and have over time become common methods to improve the rate of degradation of crude oil.

2.8.1 Temperature

The Arctic has a very short summer of only three to four months (Mohn and Stewart 2000). This leaves little time for tankers to cross the Northwest Passage safely. High traffic during this season can greatly increase the chance of a spill occurring. If a spill were to occur, this also means the clean-up response has to occur during a very short time frame. Once sea ice develops again, any major attempts of clean-up in the ocean will be impossible. The summer months are the only time that the Arctic will have temperatures above 0^0C.

The long winters may seem like a good opportunity for microbes to engage in biodegradation. However, science has shown that there is a decrease in microbial degradation when the ground is frozen. This is in part explained by the fact that microbial activity follows an Arrhenius relationship, which simply means that as temperature decreases, so does the activity of the microbes (Rike et al. 2003). Microbial activity in the winter is affected by the decrease in water content and the depletion of oxygen in the soil (Walworth et al. 2007). Nevertheless some microbial activity can still take place as long as some unfrozen water is locally available in the subsurface. Additionally, the rates of volatilization are significantly reduced as temperatures decrease (Paudyn et al. 2008).

2.8.2 Nutrients in Soil

While the addition of nutrients will have no impact on wave action, it can have a significant effect on the bioremediation of oil. Various studies have investigated the combination of nutrients that would result in the maximum microbial productivity. It was found that phosphorus and nitrogen have the greatest effect on petroleum biodegradation by microbial communities (Braddock et al. 1997). Mohn et al. (2001) found that the addition of phosphorous and nitrogen increased the microbes' ability to mineralize petroleum products. However, the addition of the nutrients only

resulted in an increase in bioremediation of specific hydrocarbons. Hydrocarbons that are composed of six or more carbon atoms (higher molecular weight) did not seem to show increased biodegradation rate).

Braddock et al. (1997) showed that different rates of nutrient addition to soil samples affect microbial activity. That nitrogen is the most important nutrient to add to soil to stimulate microbial activity but to much nitrogen can inhibit the microbes. They found that adding 400 mg N/kg soil inhibited the productivity of microbes when there was 3500 mg oil/kg soil. It was shown that this 400 mg N/kg soil threshold was the difference between the microbes being productive or inhibited. This inhibition is assumed to be caused by reduced water availability due to osmotic effects. Furthermore, soil could contain less moisture due to the lower precipitation rates and higher permafrost level at the sites where the study was done. The inhibition of microbes by adding too many nutrients was also seen in other studies done in the Arctic. Decreased productivity could also be accompanied by a decrease in carbon in the soil and a change in salinity (Braddock et al. 1997).

Chapter 3 Material and Methods

3.1 Materials

3.1.1 Sediment Sampling

Sediment sampling was performed from July 22nd to 25th 2013 at four different beach locations near Barrow, Alaska whose GPS coordinates are shown in Figure 5 and Table 1. Each sample was collected from the top 60 cm of sediment. Four five gallon buckets were filled with beach sediment (each containing roughly 30 kg of sediment), one from each location. Two buckets were collected along the Beaufort Sea/Elson Lagoon, where the sediment had a more sandy-gravel composition (4-ESI). Two buckets were collected along the Chukchi Sea, these sediments were primarily composed of pebble material (5-ESI). The samples were transported back to the laboratory and kept at 4°C. An ocean water sample adjacent to each site was also collected and brought back to the laboratory to identify the salinity of the water. The samples were analyzed using a conductivity meter, and the determined salinity was 30 g/L.

The two buckets of each sediment type were combined into one bucket (Sandy-Gravel and Pebble) these were then used to determine the fate of crude oil for a variety of conditions both in mini-column and wave tank studies. For the remainder of the paper, the two sediment types will be referred to as sandy-gravel and pebble respectively.

Table 1: GPS Coordinates of Sampling Locations

Sample Number	Latitude	Longitude
Sandy-Gravel 1	71°21'34.91"N	156°21'42.74"W
Sandy-Gravel 2	71°21'39.80"N	156°21'47.90"W
Pebble 1	71°23'2.99"N	156°29'7.13"W
Pebble 2	71°17'11.00"N	156°48'29.12"W

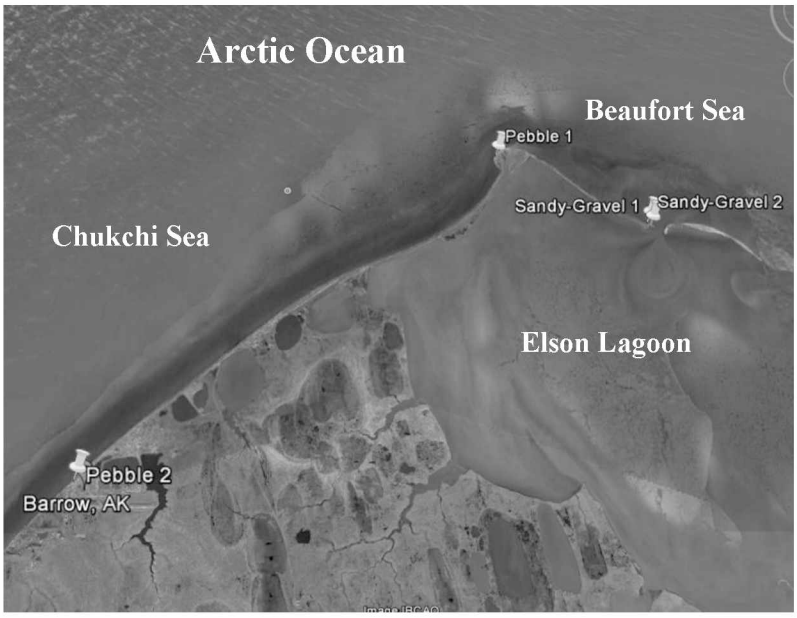

Figure 5: Sampling locations.

3.1.2 Preparation of Solutions

Before the start of the experiment, all solutions needed for the experiment were created. Sea water with a salinity of 30 g/L was created using *Instant Ocean Aquarium Salt,* which had concentrations of 3.6ppb NH_4, 12.4ppb NO_3, and 19ppb PO_4 (Atkinson and Bingman 1997). In a five gallon bucket, the salt was added to tap water until a salinity of 30 g/L was achieved. After a batch of artificial seawater was used up, a new solution was made. All salinity readings were between 29.5 g/L and 30.5 g/L.

Two different methods of adding fertilizer were used during the course of the experiment. For both methods a fertilizer with a $N/P_2O_5/K_2O$ ratio of 20/20/20 was used, whereby the 20% nitrogen were made up of 20% ammonia, 30% nitrate, and 50% urea nitrogen. The liquid fertilizer solution was created by dissolving the fertilizer in water to achieve a final concentration of 30 mg N/ml of solution. The solid fertilizer was simply the same fertilizer in its original fine powdered form.

3.2 Overview of Laboratory Studies

Two different experimental designs were implemented to help understand how the sediment composition affects the transport and oil biodegradation rate. A microcosm study was done using a mini-column set up. This helped to provide an in-depth look at the transport of oil through the sediment profile, simulating the rise and fall of the tides. A wave tank was used as a scale model of a shoreline environment.

3.3 Mini-column Studies

3.3.1 Overview

The purpose of these experiments was to study biodegradation and transport of crude oil through the sediment. Mini-columns were filled with sediment, crude oil was added, and several flushing cycles were performed to simulate tidal action. After different experimental durations, the petroleum hydrocarbons at different depth within the column were measured. The amount of hydrocarbons evaporated was determined by measuring volatiles collected in activated carbon, and the amount of CO_2 released was determined by titrations of NaOH. Temperature, sediment type, and the addition of liquid or solid fertilizer were varied for the experiment.

3.3.2 Construction of Mini-Columns

Mini-columns were constructed using PVC pipe, as shown in Figure 6. A 1½ inch ABS PVC-pipe was cut into 18 inch long sections. A 1½ in ABS adapter fitting and threaded plug fitting was attached to each end. A threaded ¼ inch hole was drilled into the plug fitting, and a barbed nylon national pipe thread (NPT) was threaded into place. ABS cement was then used to seal the adapter fitting and barbed nylon into place, to ensure no water could leak out.

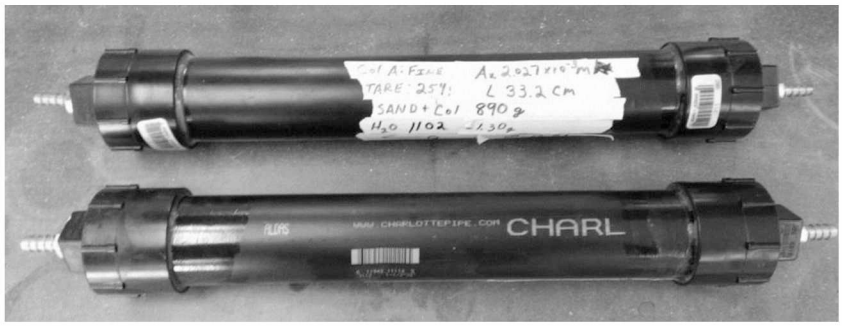

Figure 6: Column design used in experiment.

3.3.3 Experimental Design

Two different preliminary experiments were performed to determine the best experimental conditions for subsequent studies, such as the duration between each flush, or the number of flushes that caused substantial movement of crude oil through the profile. The first experiment involved varying the time between each flush, with the same number of flushes (six) in each of three experiments. The first lasted 6 hours where the system was flushed every hour. The second was over 48 hours, and the system was flushed every 8 hours. The last took 72 hours, and the system was flushed every 12 hours.

The second experiment varied the number of flushes using a standard time of 12 hours between flushes since tidal cycles are generally 12 hours apart. As a 3 day trial had already been run, two additional studies were run for durations of 6 and 12 days, with a total of 12 and 24 flushes respectively.

A comparison of these two preliminary experiments was done to determine which factor (time between flushes or number of flushes) would be most influential. It was concluded that the number of flushes, not the timeframe in between the flushes had a greater impact on the overall movement of the oil.

Titration data showing the amount of CO_2 released also yielded some interesting results, with no difference in the release of CO_2 between the control column (without crude oil addition) and the columns with crude oil added. Two possible explanations for this were that since the experiment used actual soil collected from Barrow, a carbon source must have been present in the soil. Another possible explanation was that the liquid fertilizer was rinsed out so fast that it did not have a sufficiently long residence time in the column to actually have an impact. For this reason it was decided to conduct an additional experiment of 18 days and add an additional column with solid fertilizer. Therefore the three remaining experiments would have a control (without crude oil), crude oil with liquid fertilizer, crude oil with solid fertilizer, and crude oil with no fertilizer as shown in Table 2. These experiments were ran for 3, 6, 12 and 18 days, with flushes every 12 hours.

3.3.4 Methodology for Mini-Column Experiments

The procedure of the mini-column experiment is schematically shown in Figure 7. Seven columns with conditions as described in Table 2 were used in each experimental run, with duplicate columns for all experimental conditions except for the control. Experiments with durations as specified in Table 3 were performed with 7 columns each at 3°C and 20°C.

Table 2: Conditions in Each Column Experiment

PVC Pipe	Oil	Liquid Fertilizer	Solid Fertilizer	NaOH	Activated Carbon
1a	Yes	No	No	Yes	Yes
1b	Yes	No	No	Yes	Yes
2a	Yes	Yes	No	Yes	Yes
2b	Yes	Yes	No	Yes	Yes
3a	Yes	No	Yes*	Yes	Yes
3b	Yes	No	Yes*	Yes	Yes
4	No	No	No	Yes	Yes

* Note: for the 20°C sandy gravel study no solid fertilizer was used

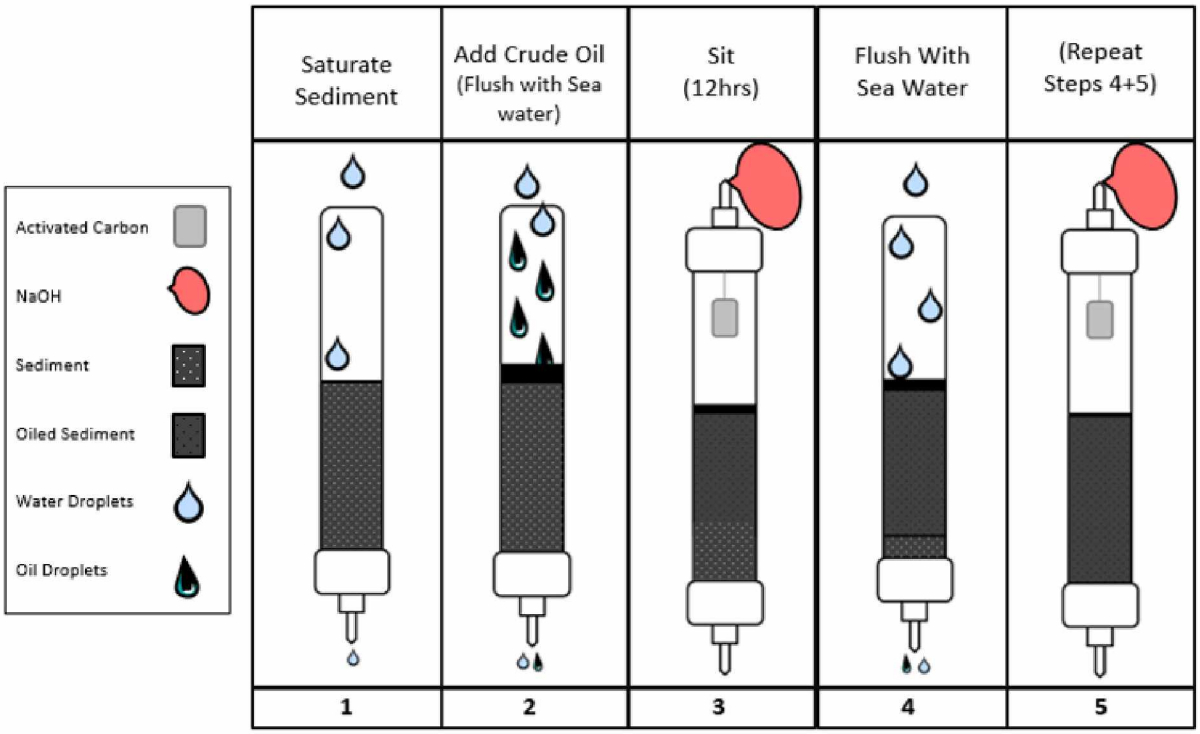

Figure 7: Mini-column experimental set-up.

The procedure for the mini-column experiments was as follows:

1) Seven PVC pipes were each filled with approximately 400 g of sediment mixture up to a height of 12 inches and placed on shaker table to compact the sediment to simulate ocean beaches.
2) From the top the sediment was saturated with water. Once saturated, the bottom of the column was opened to drain excess water. In future studies the columns should be filled from the bottom up, to ensure there is no entrapped air.
3) Two ml of crude oil was introduced from the top to PVC pipes 1a, 1b, 2a, 2b, 3a, and 3b,
4) Twenty ml of liquid fertilizer with nitrogen concentration of 30 mg/mL was then added to column 2a and 2b.

5) Solid fertilizer was added to columns 3a and 3b to achieve a dosage of 600 mg of nitrogen per column.
6) PVC pipe 4 is used as a control with no fertilizer or oil added.
7) 50 ml of salt water was added from the top and allowed to drain out completely.
8) Once water drained out, the bottom valve was shut allowing no more water or oil to exit the column.
9) A "tea bag" filled with ~1.5 g of activated carbon was suspended in the air space of the tube. The same "tea bag" would be used for the entire course of each experiment, to determine the total volatiles released over the specific time frame.
10) A clear balloon filled with 20 ml of 1 N NaOH solution was attached to the cap of the PVC-pipe, ensuring that no air can escape. The same NaOH was used for the entire experiment. After the 18 day experiment, it was clear from titrations, that the NaOH was still able to absorb CO_2, so no loss of CO_2 was believed to occur.
11) The top of the column was sealed using plumbers tape wrapped around the thread cap tightly fitted to the top of the column, so no air could escape.
12) After allowing the system to sit for 12 hours, the NaOH balloon and activated carbon were removed and then Steps 7-12 were repeated for the remaining flush cycles, with experimental durations of 3, 6, 12 or 18 days, as shown in Table 3.
13) After the last cycle, the bottom end of the PVC pipe was opened and allowed to sit for 30 min. The NaOH balloon and activated carbon were removed, to be analyzed as described in section 3.5.1 and 3.5.3. One composite sediment sample was taken from the top, middle and bottom of the column, each approximately 10 g. The samples were stored in amber vials at -80°C until analysis as described in section 3.5.2

Table 3: Experimental Time Frame

Time between flushes (hrs.)	Number of Flushes	Number Days
12	6	3
12	12	6
12	24	12
12	36	18

3.4 Wave Tank Study

The wave tank was used to simulate how the crashing of the waves on the shore affects movement of the oil through the sediment horizon. There was no data collection for this experiment, it was strictly an observation.

A plexiglass tank was purchased with the dimensions of 5×1.5×2 ft. In order to test both sediments under identical conditions, a plexiglass divider was installed, so both sediment types could be evaluated simultaneously. Sediment was placed into the tank creating a slope of approximately 30 degrees (Appendix B, Figures 30, 31, 34a). The sediment was approximately 12 inches high and extended 20 inches on the tank's bottom as shown in Figure 8.

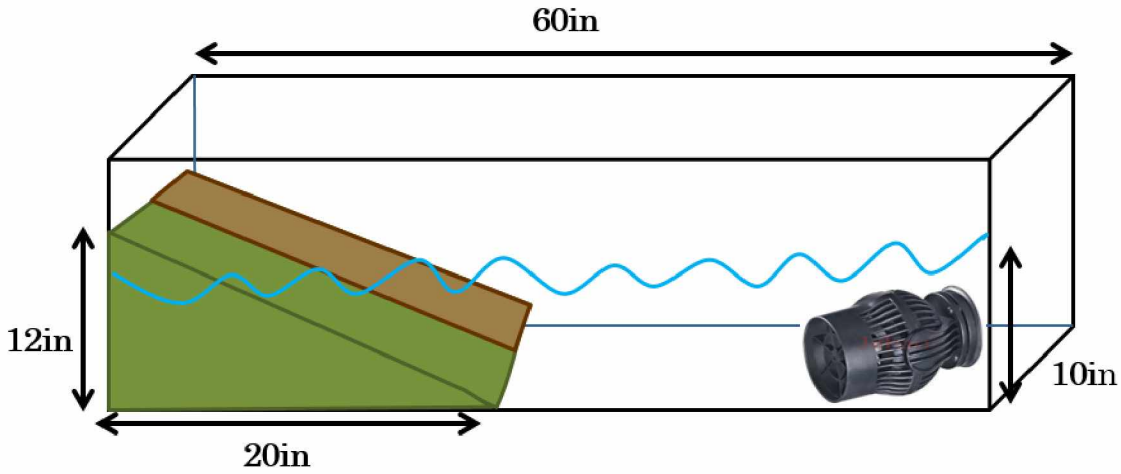

Figure 8: Wave tank schematic.

The tank was filled with 10 gallons of artificial salt water mixture (Appendix B, Figure 32, 34b). After allowing the water to completely saturate the sediment (~ 30 min), a wave maker (Jebao WP-40, 900 to 3400 GPH) was used to generate a consistent wave pattern (Appendix B, Figure 33). Once the wave generation has stabilized, 20 ml of crude oil was added to the end of the tank, and 5 mL was added straight to the shoreline. The 20°C and 3°C experiment was conducted over 3 days with continuous wave action (Appendix B, Figure 34c). At the end of the study, the wave simulator was turned off. After 30 min, the water was slowly drained from the tank. Samples were collected, but could not be analyzed. Therefore this study was strictly observational.

3.5 Analysis

For mini-columns, total petroleum hydrocarbon remaining in the sediment, released CO_2, captured in NaOH solution (indicating hydrocarbon mineralization) and volatilized hydrocarbons captured in activated carbon were analyzed.

3.5.1 Porosity Test

Porosity was determined by filling a beaker with a known volume (V_T) of sediment. The sediment was placed on a shaker table for 5 minutes to ensure proper settling. The sediment and beaker were then weighed and the value recorded. The beaker containing the sediment was then filled with water until it was completely saturated and re-weighed. The volume of water added equals the volume of voids (V_V). The porosity was then determined as V_V/V_T.

3.5.2 Titration - CO_2 Release

The method used for quantifying carbon dioxide release was adapted from Crossno et al., (1996). As this is a time sensitive procedure, titration was performed immediately after removing the balloon. For each column, the balloon filled with NaOH was transferred into its own beaker. 10 mL of $BaCL_2$ and 1 drop of 1% phenolphthalein solution (color indicator) was added to the beaker.

Using a Metrohm Titrino, 1 N HCl solution was titrated until the solution changed from pink to clear. The amount of HCl added was recorded. Using the following formula, the mass of CO_2 released (mg) was determined.

Volume of titrant (ml) × molarity of acid × MW of CO_2 = mass of CO_2 (mg)

3.5.3 Gas Chromatography/Flame Ionization Detection (GC-FID)

Upon the completion of the column study, sediment samples were collected and stored at -80°C until analysis. At the start of analysis, samples were removed from the freezer and allowed to warm up slightly before extraction. Crude oil was extracted using 25 ml of methylene chloride and 250 µL of 2190 mg/L D-8 naphthalene (surrogate), and placed on a shaker table for 90 minutes. The liquid mixture (crude oil, D-8, and methylene) was removed and placed in a clean amber vial. 1.5 ml of liquid was then placed into a GC vial, and 10 µL of D-5 nitrobenzene (internal standard) was added. The samples were analyzed on the GC-FID, following a modified diesel range organics (DRO) AK 102/103 method (ADEC, 2002a, 2002b, 2002c).

The GC-FID was an Agilent Technologies 6890N Network (flame ionization detector), with a 30 m by 250 µm by 0.25 µm column. The oven was set at an initial temperature of 40°C and increased to 350°C over a 34.50 minute duration. A pulsed split-less injection was used with hydrogen or helium as gas carriers, helium replaced hydrogen halfway through the experiment, as it is a safer, less flammable gas. The only change in the data was a slight difference in retention time, otherwise no impact on data reliability was seen. This was determined by running a calibration curve and comparing it to the previous carrier gas data. The carrier gases were set at a pressure of 20 psi, flow of 12.4 ml/min, and an average velocity of 15.2 cm/sec.

Standards were prepared in a range of 250-2500 mg/L. The density of the crude oil was found to be 867 mg/ml (20°C) and 873 mg/ml (3°C), with a viscosity of 43.6 cP (20°C) and 104 cP (3°C). Two ml i.e. 1,740 mg of crude was added to each column.

The total chromatogram area from 4-24 minutes was used for calculating the crude oil concentration. From the standards, a calibration curve was created, to quantify total petroleum hydrocarbons for each sample. The average TPH concentration of the two replicate columns was calculated and is reported in the results section. Error bars in figures show a standard percent deference of five percent, this value was the maximum percent difference found between the duplicate columns throughout the experiment.

3.5.4 Gas Chromatography/Mass Spectrometry (GC-MS)

At the completion of each column study the activated carbon was removed from the columns, and placed on a clean surface. 0.5 g of activated carbon was then measured into individual GC vials, the vials were labeled and stored at -80°C.

When the samples were ready for analysis, the vials were removed from -80°C, and allowed to defrost. The caps were removed and 1 ml of carbon disulfide was added to each vial. 5 µL of the internal standard of 2500 mg/l of heating fuel in carbon disulfide was added to each vial. The vials were immediately placed on the GC-MS for analysis.

The samples were analyzed on an Agilent Technologies 6890N Network GC-MS, with a JW 123-1062, 60 m by 250 µm by 0.25 µm column. The oven was set at an initial temperature of 150°C and increased to 350°C over 16.50 minutes. Using a split-less injection with helium as a carrier gas at a pressure of 9 psi, flow of 1.6 ml/min, and an average velocity 3.2 cm/sec.

During the analysis process, the GC/MS encountered some technical difficulties and shut down numerous times, requiring that the samples be re-analyzed. Throughout the analysis, the machine was checked multiple times, and multiple sample runs were performed to ensure the machine was working correctly. After analysis, it was however determined that the equipment malfunctioned and multiple samples were not analyzed or only analyzed for half of the required time, leaving over a quarter of the data unusable.

Chapter 4 Results and Discussion

The purpose of the study was to understand the fate of crude oil in different shoreline substrates. This chapter will be broken up into several sections. The first section discusses sandy gravel sediment, followed by pebble sediment, and finally a comparison of sandy gravel versus pebble. In each case, two temperatures and different fertilizer types are compared to determine their effect on the fate of crude oil.

For all of the above conditions (different sediment types, temperatures and fertilizer application), the crude oil degradation and transport were evaluated by measuring three parameters: the concentration of crude oil throughout the column profile, the CO_2 production, and the release of hydrocarbon volatiles. As mentioned in the analysis section, some errors occurred in the analysis of volatiles captured by the activated carbon, which resulted in too many data gaps to consistently quantify the release of hydrocarbons. Therefore the activated carbon data will not be discussed in this chapter, only the change of crude oil concentration throughout the column and CO_2 production will be discussed.

It should be noted that for all graphs showing the crude oil concentration, the control columns are not included because the hydrocarbon concentration was consistently very low, i.e. 1-2 mg/kg for all experiments. The data for the controls without crude oil addition can be found in the Appendix A.

The wave tank portion of this study was strictly observational since no hydrocarbon data could be recorded. Photos of the experiment can be found in Appendix B.

4.1 Sandy Gravel Sediment

The sandy gravel samples were composed of coarse grain sand and some gravel with the porosity determined to be 0.36. As mentioned in the methods, the sandy-gravel study at 20°C was completed first, for durations of 3, 6 and 12 days, without columns with addition of solid fertilizer. Upon the completion of this study, it was clear that more time should be allowed and that a solid fertilizer should be added to reduce fertilizer wash-out. Consequently, for the sandy gravel study at 3°C additional experiments were performed with a duration of 18 days, and including columns with solid fertilizer. The lower temperature of 3°C is more indicative of conditions in Barrow, and the majority of the Arctic shoreline.

4.1.1 Crude Oil Movement

Figures 9 and 10 seen below show the average crude oil concentration at different places in the column for the 20°C and 3°C studies respectively.

At 20 °C it is notable that all sandy gravel columns follow the same general trend. A much higher concentration of crude oil resided in the middle section of the column, about 6 inches below the surface. This result is consistent with the classification as ESI 4, which has an expected max oil penetration of 25 cm (10 in) (NOAA, 2004).

For most days, a higher concentration of crude oil in the columns was noted when no fertilizer was added. The crude oil concentration in the column with no fertilizer showed a consistent downward trend over time for the top and middle of the column, with concentrations consistently highest in the middle.

The liquid fertilizer follows the same trend with highest concentrations observed in the middle of the column followed by the bottom of the column and lowest concentrations at the top. The

increase in TPH at the top of the column from day 3 to day 6 must have been a sampling error on either day 3 or 6. There was an initial decline in TPH from 0 to 3 days, but from 3 to 12 days very little additional decline in crude oil concentration was seen. It therefore appears that the addition of fertilizer did not have a significant impact on the degradation of crude oil after 3 days. This can be attributed to the fact that the fertilizer was in liquid form and most likely washed through the entire column by day 3.

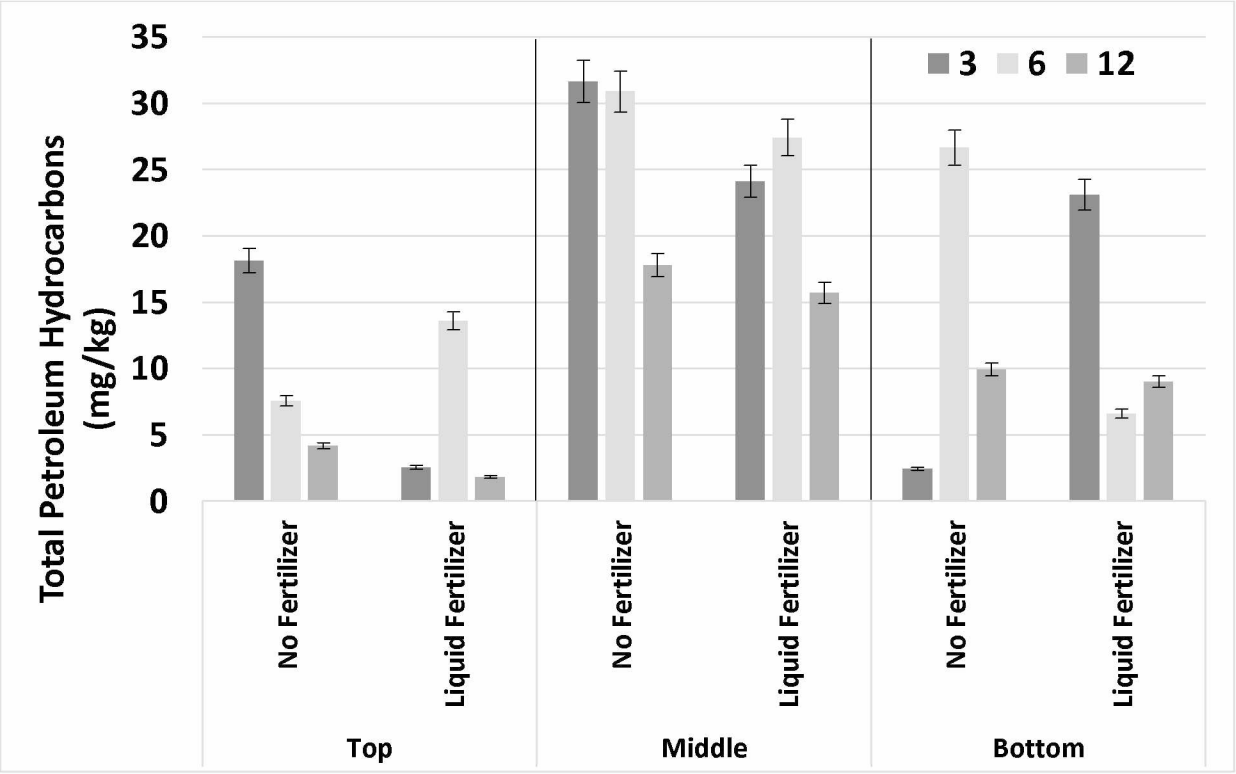

Figure 9: TPH concentration at different depths after 3-12 days in sandy gravel at 20°C. Error bars represent standard percentage error of 5% for the duplicate columns

Crude oil concentrations at 3°C did not follow such a clear trend as seen at 20°C. The data were more scattered. In unfertilized columns, the maximal crude oil concentration occurred in the middle of the column. It also appears that past day 6, there was no significant decrease in crude oil concentration at the top of the column, with nearly identical concentrations on day 6, 12, and 18,

indicating that no further movement from the top of the column occurred through the sediment. Over time, the average crude oil concentrations slowly decreased but removal did not occur to the same extent as at 20°C.

In columns with liquid or solid fertilizer, either the top or the middle of the column showed the highest TPH concentrations. Similar to 20°C the crude oil concentrations decreased over time, but it does not appear that fertilizer addition played a role. With solid fertilizer, average TPH concentrations decrease at a very slow rate. The concentration at the top of the column remained consistently high. By day 18, the columns with solid fertilizer had the highest crude concentration at any level.

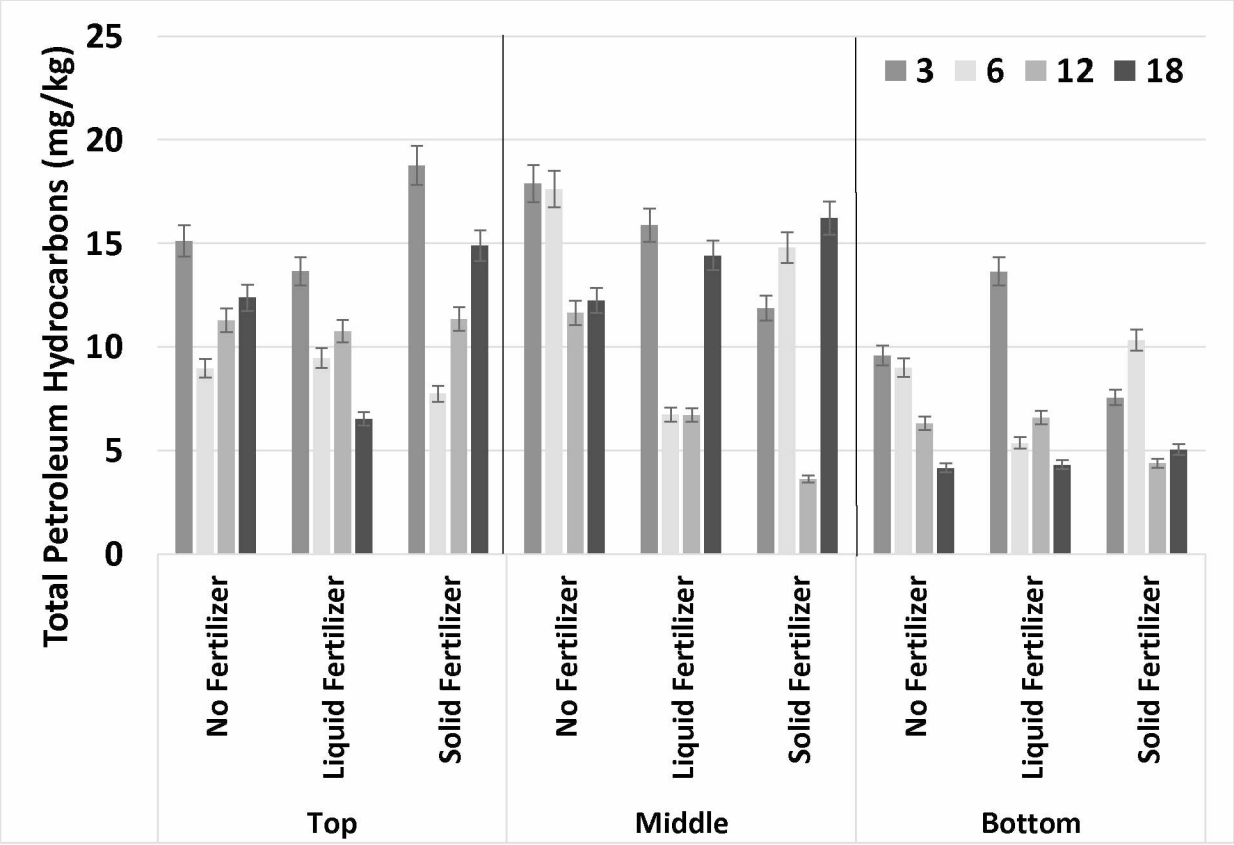

Figure 10: TPH concentration at different depths after 3-18 days in sandy gravel at 3°C

Error bars represent standard percentage error of 5% for the duplicate columns

4.1.2 Carbon Dioxide Release

Figure 11 and Figure 12 show the average cumulative amount of CO_2 that was released from each of the columns over 3, 6, 12, and 18 days for 20°C and 3°C respectively. Respiration data at 20°C followed the general expected trend, with a steady increase in CO_2 produced over time. Day 3 and 6 show nearly identical respiration for all 3 conditions, i.e. there was no noticeable effect of crude oil or nutrient addition. The similarly high CO_2 release without crude oil addition indicates that there must have already been a carbon source present in the soil; a similar finding was made Sharma, 2015. For the first 6 days, the microbes present in the soil were still utilizing the original carbon source and had not yet begun to degrade the crude oil. By day 12, the original carbon source had been used up and the microbes moved on to the crude oil allowing them to release an additional 20-40 mg of CO_2. It is interesting to note that the liquid fertilizer does not appear to have as positive an impact on the release of CO_2, as was expected. As mentioned before, this could be due to the fertilizer being flushed out of the system early on, and therefore no longer being present by day 12 when crude oil utilization started. It should be mentioned that throughout the experiment, the columns were flushed with sea water, which means that along with a higher salinity, there were also nutrients present in the water as specified in section 3.1.2. So it is possible that the simple addition of sea water to the system was enough to stimulate the microbes. It is still unclear though, why the columns with no fertilizer addition released so much more CO_2.

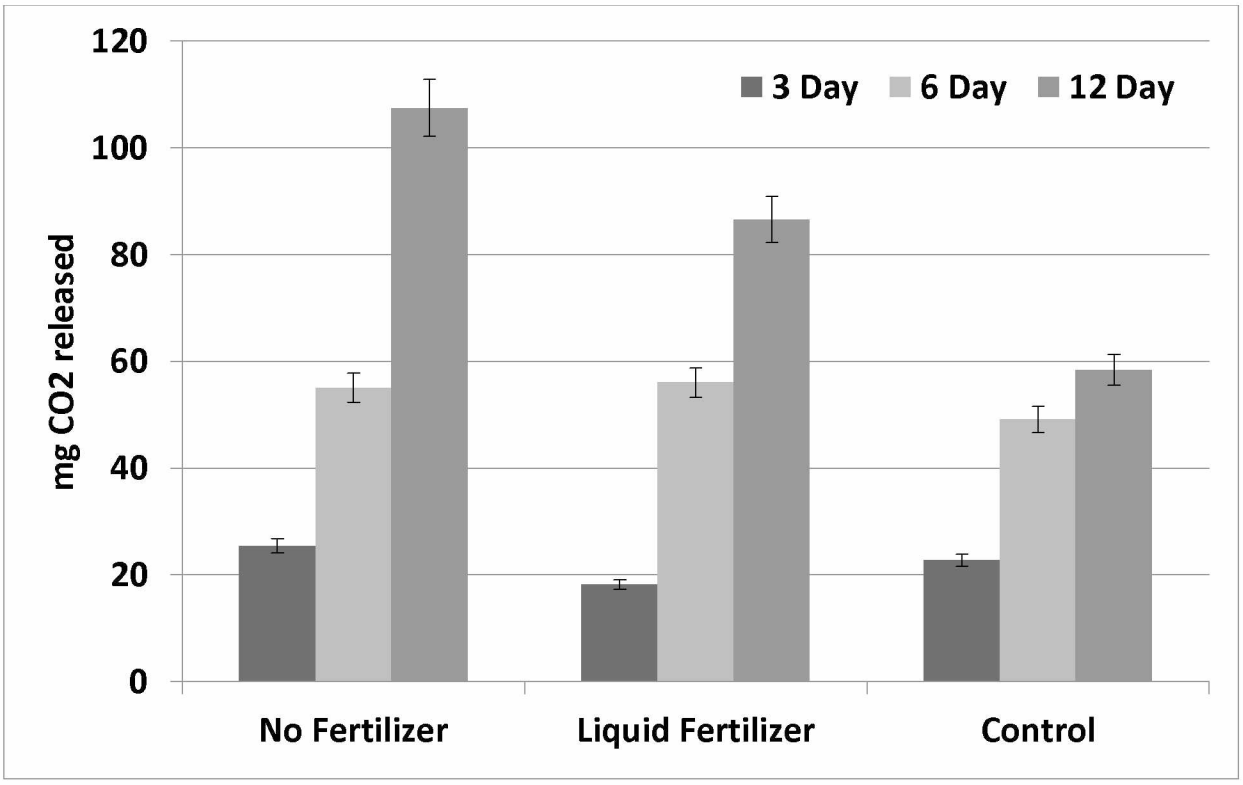

Figure 11: Cumulative CO_2 released from sandy gravel at 20°C
Error bars represent standard percentage error of 5% for the duplicate columns

The CO_2 production from sandy-gravel at 3°C shows a similar trend as in the 20°C study, where independent of fertilization and crude oil addition almost the same amount of CO_2 was released for day 3 and 6 (in the 20°C study a nearly identical release was also seen at day 12). It is not until day 18 that a significant spike in CO_2 release due to crude oil degradation is seen. This longer lag time can be attributed to the lower temperature. It is known that as temperature decreases, microbes slow down their metabolism rate, and therefore do not need to consume their energy source at as quickly (Horel, 2009). It is important to note that the control on day 18, while it is higher than on day 12, is nearly 40 mg less than the columns that contained crude oil. This indicates that somewhere between the 12^{th} and 18^{th} day, the microbes finally depleted the sediments original carbon source, and moved on to the crude oil. Similar to the 20°C study, the addition of fertilizer

does not seem to play a significant role in the release of CO_2. While at day 18, we do see a slightly higher release with the addition of solid and liquid fertilizer, it is by less than 15 mg higher than in the unfertilized column. As mentioned earlier it is possible that the sea water is contributing sufficient nutrients to the microbes, and that the addition of fertilizer would be unnecessary.

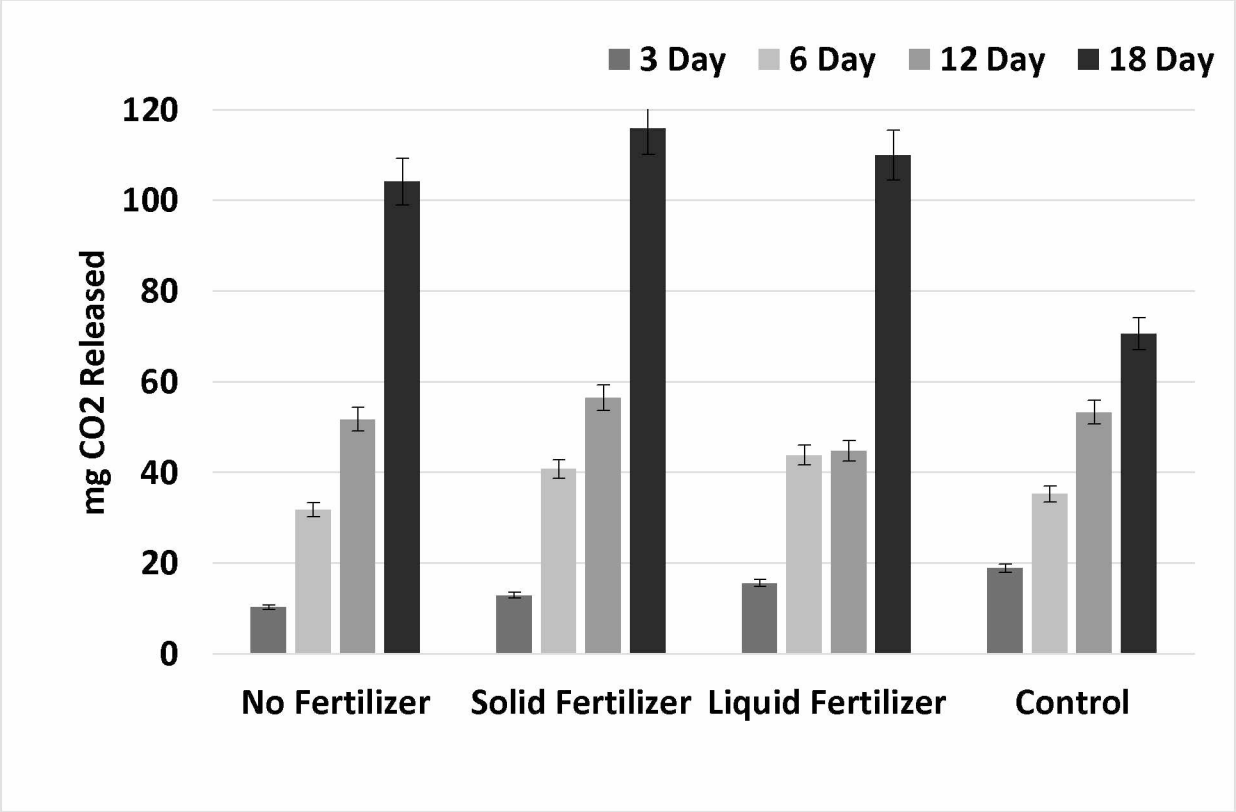

Figure 12: Cumulative CO_2 released from sandy gravel at 3°C
Error bars represent standard percentage error of 5% for the duplicate columns

4.1.3 Effect of Fertilization & Temperature

The temperature seems to have a significant effect on the TPH degradation and CO_2 production. As the 20°C study did not include experiments up to day 18 or solid fertilizer, this comparison only shows how the columns with no or liquid fertilizer compared at the two different temperatures. Figures 13 and 14 show crude oil concentrations for varying temperatures, without fertilizer addition and with liquid fertilizer, respectively. For both figures, it appears that more

crude oil was recovered from the soil at the higher temperature. At 20°C, there is a fairly clear trend of crude oil moving through the column, with only little TPH present in the top layer after day 6. TPH concentrations overall decreased with time, but were nevertheless on average still higher than at 3°C. At 3°C the concentration after three days was already relatively low and decreased only slightly over time. One explanation for this apparently quick loss of TPH in the first three days at 3°C could be that an initial movement of crude oil through the system led to removal of crude oil. However, considering the lower viscosity at low temperature that appears unlikely. Another possible explanation could be that the 20°C samples were extracted and analyzed within a week of the completion of the experiment. Whereas, the 3°C samples were stored in the -80°C freezer for about 3 weeks (up to 31 days), before extraction and then due to machine malfunction had to be stored for another 4 weeks (up to 40 days) before analysis could be completed. While extraction and analysis where both within the required time frames, they did have a slightly lower crude oil recovery from soil, but still within the recommended recovery rate.

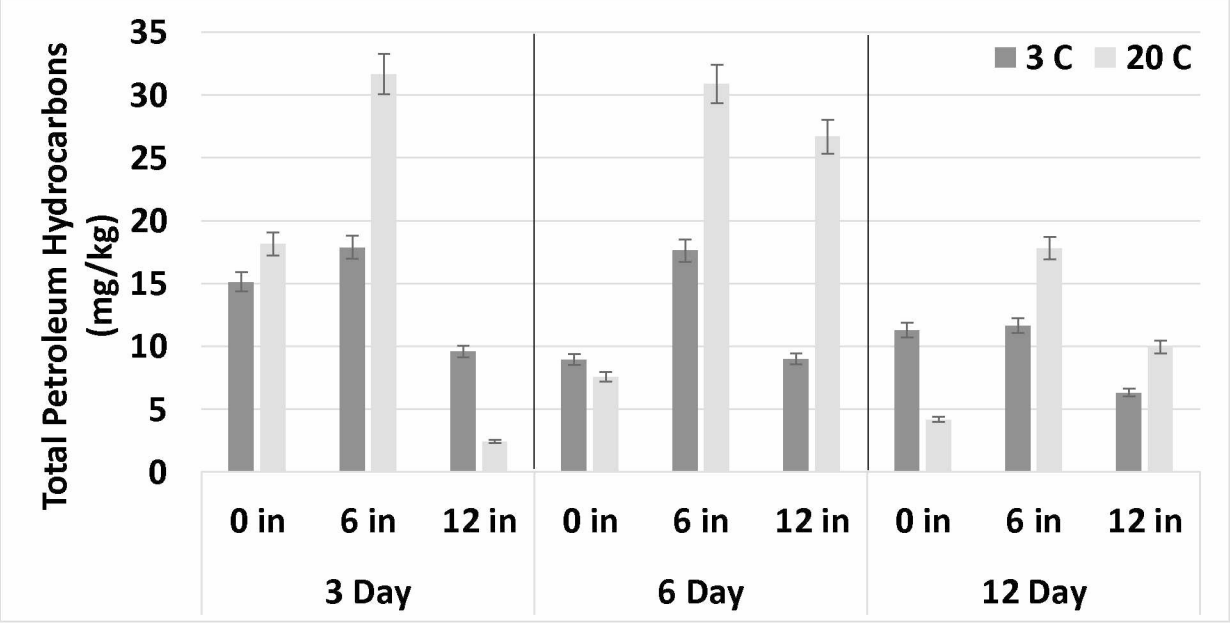

Figure 13: Effect of temperature on TPH concentrations in samples without fertilizer

Error bars represent standard percentage error of 5% for the duplicate columns

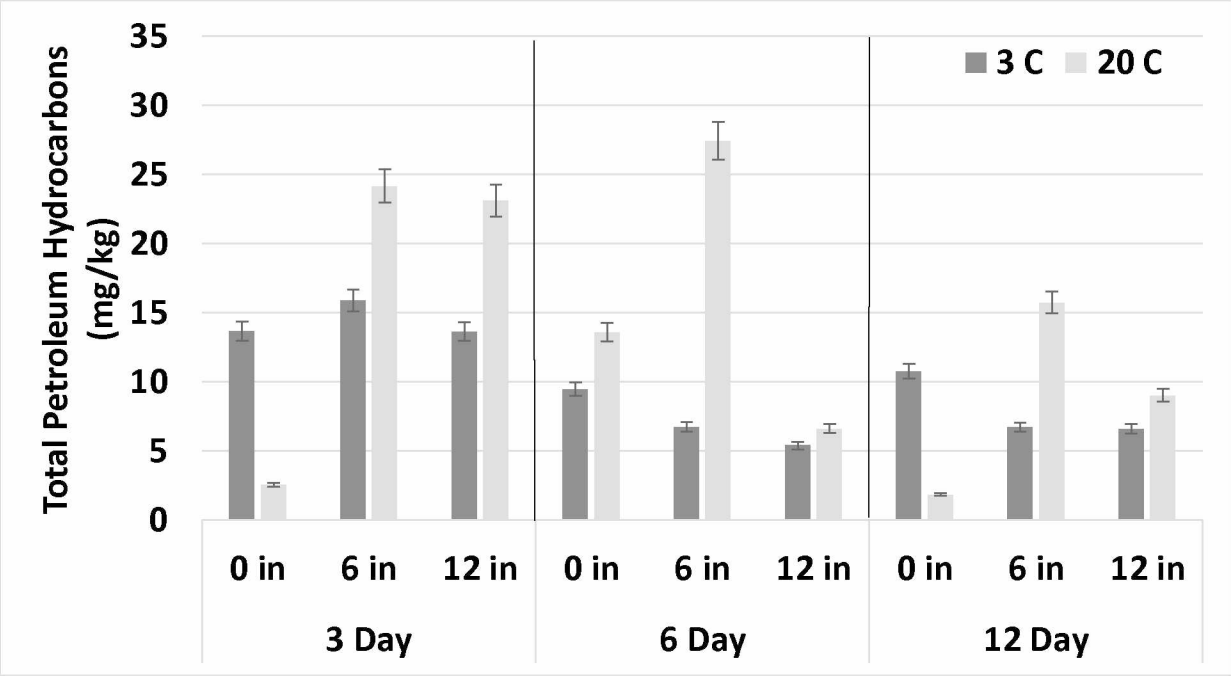

Figure 14: Effect of temperature on TPH concentrations in samples with liquid fertilizer
Error bars represent standard deviation (duplicate columns)

Figure 15 shows how the temperature affected the release of CO_2 in sandy gravel sediment. For any time period, there was a higher release at 20°C than at 3°C. It is normal for microbes to be more active at higher temperatures than at lower temperatures. Nevertheless this is interesting as the locally present microorganisms would be more adapted to low temperatures and perform well at those. The majority of the Arctic rarely reaches air temperatures of 20°C, and the average summer temperature is around 5°C. It can be extrapolated from the data that if an 18 day study at 20°C had been completed, the CO_2 release would have been much larger than the 110 mg that were released at 3°C.

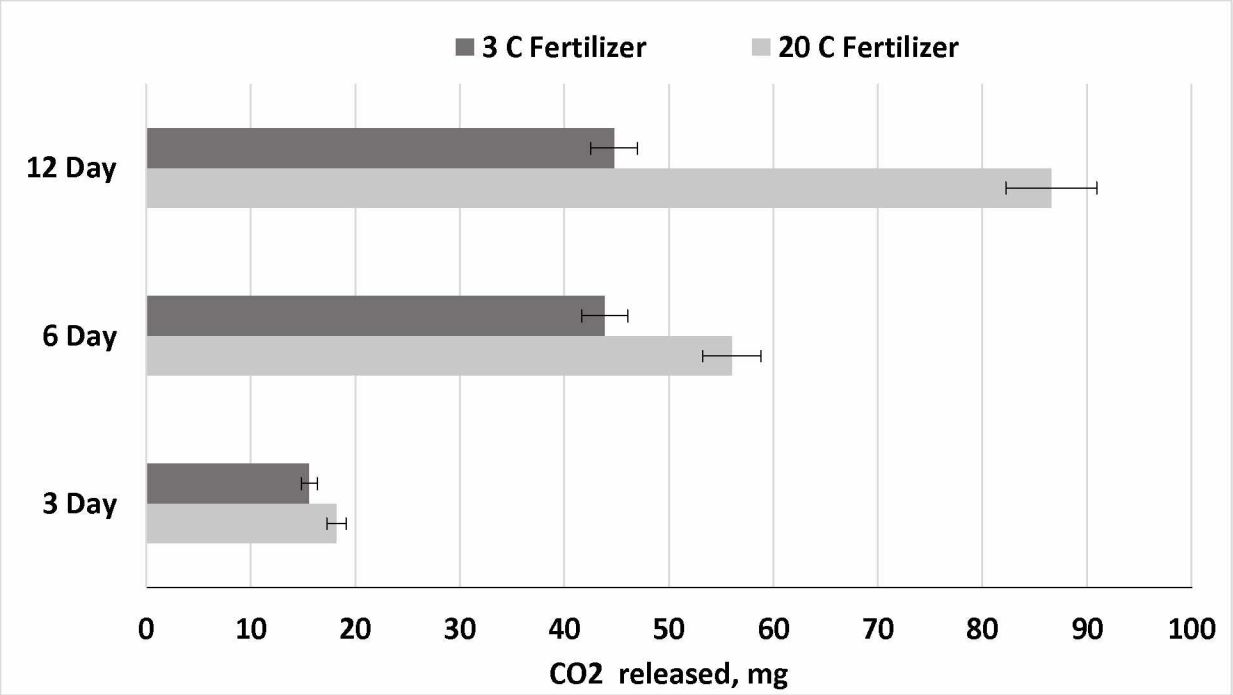

Figure 15: Effect of temperature on release of CO_2 from sandy gravel with liquid fertilizer

Error bars represent standard percentage error of 5% for the duplicate columns

4.2 Pebble Sediment

The pebble sediment, characteristic of ESI 5, was comprised of a mixture of pebbles with some sand. The porosity for the sample was determined to be 0.31. It had a medium to high permeability, with a high chance of oil penetration up to 20 inches (NOAA, 2004).

4.2.1 Crude Oil Movement

Figures 16 and 17 show the average crude oil concentration at different locations in the column for the 20°Cand 3°C studies respectively. A similar trend is seen at both temperatures, with a higher crude oil concentration at the top (0 in) and the bottom (12 in), and the lowest concentration in the middle. At 20°C it appears that the movement of crude oil is consistent with the ESI 5 rating. Already on Day 3, a high concentration of crude oil was observed not only at the top but also at the bottom of the column, indicating that significant transport had occurred during that short time period, i.e. the crude oil moved freely through the column. By day 6, the concentration at all levels, but especially at the top had decreased, indicating that, the majority of crude oil (~ 3 mg/kg remain) had been removed from both the top and middle layers of the column. This removal could have been due to volatilization and/or biodegradation (discussed below in section 4.2.2). The upper two layers showed a further slight decrease in concentration over the next 12 days, with a residual concentration of approximately 2 mg/kg. At the bottom of the column, a relatively high concentration was still present at day 6 and 12, indicating some pooling may have occurred. By day 18, the entire column exhibited the same low crude oil concentration, i.e. the majority of crude oil was removed from the system, and the soils approached the TPH concentrations in the control without oil addition (2.4-1.7 mg/kg). TPH removal from the bottom layer may have been due to crude oil slowly being washed out of the column over time. In real life crude oil may be washed

back out into the ocean. There was little impact of fertilization on TPH levels, the fertilizer may have been washed out.

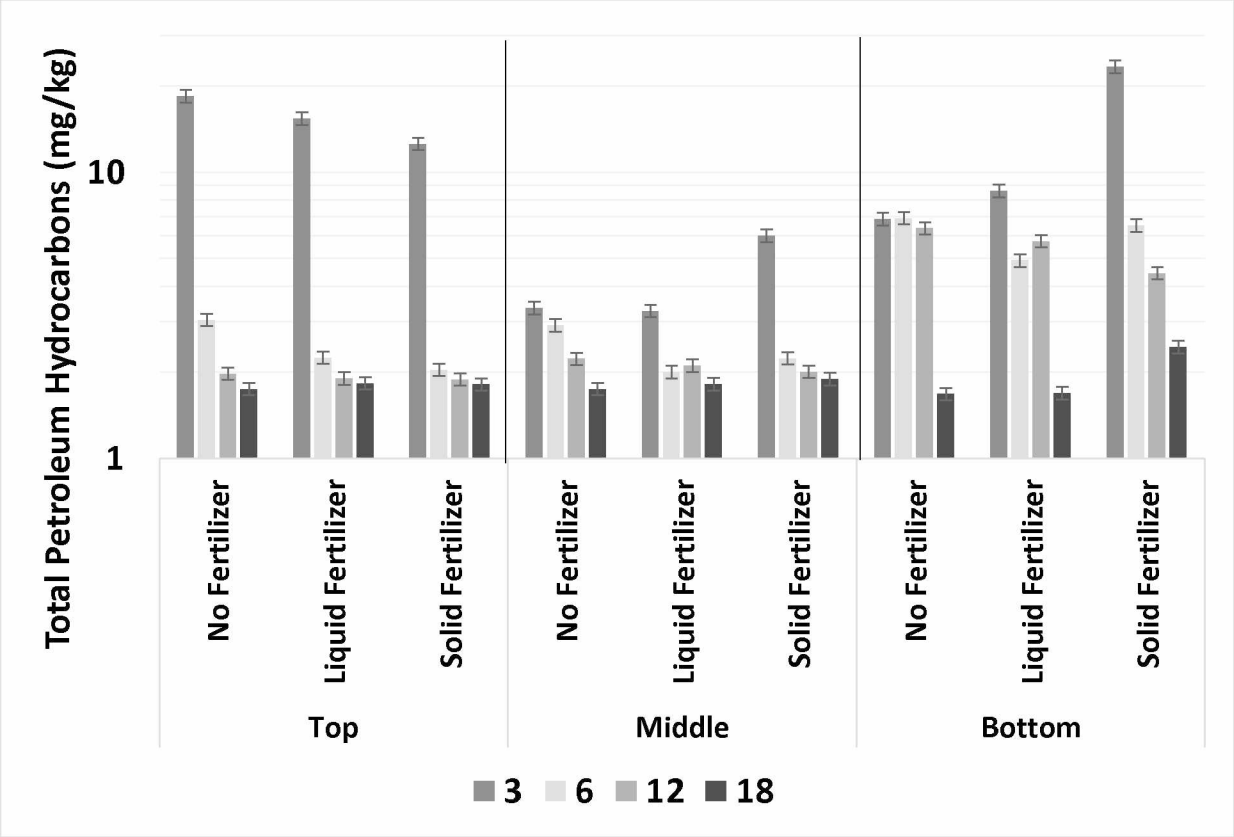

Figure 16: TPH concentration at different depths after 3-12 days in pebble sediment at 20°C. Error bars represent standard percentage error of 5% for the duplicate columns

The same trend was seen at 3°C. The top and bottom of the column had a very high concentration at day 3. At the top, this concentration quickly dropped by day 6 to about 2 mg/kg and remained at that level for the remainder of the study. After three days, the middle of the column showed concentrations (4 mg/kg) that were lower than at the top or bottom. Over the next 12 days, concentrations in the middle slowly decreased to a final concentration of 2 mg/kg. As in the 20°C study, the bottom of the soil maintained a fairly high, but decreasing, concentration for the first 12 days. By day 18, pooling at the bottom no longer occurred, and the entire column exhibited the

same generally low concentration of 2 mg/kg which is comparable to the control concentration (2.4-1.7 mg/kg). This means at the lower temperature, the crude oil had been largely removed from the column over the 18 day duration.

As in the 20°C pebble study, the addition of fertilizers did not cause a large effect on TPH levels in the column. However, at 3°C, it appears that especially the solid fertilizer enabled TPH removal at a slightly faster rate.

Considering that concentrations at the top and bottom of the pebble column were higher than in the middle, the question arises whether some fractions of hydrocarbons may have been transported more easily towards the bottom while heavier fractions remained at the top. However GC spectra did not show evidence of such fractionation occurring.

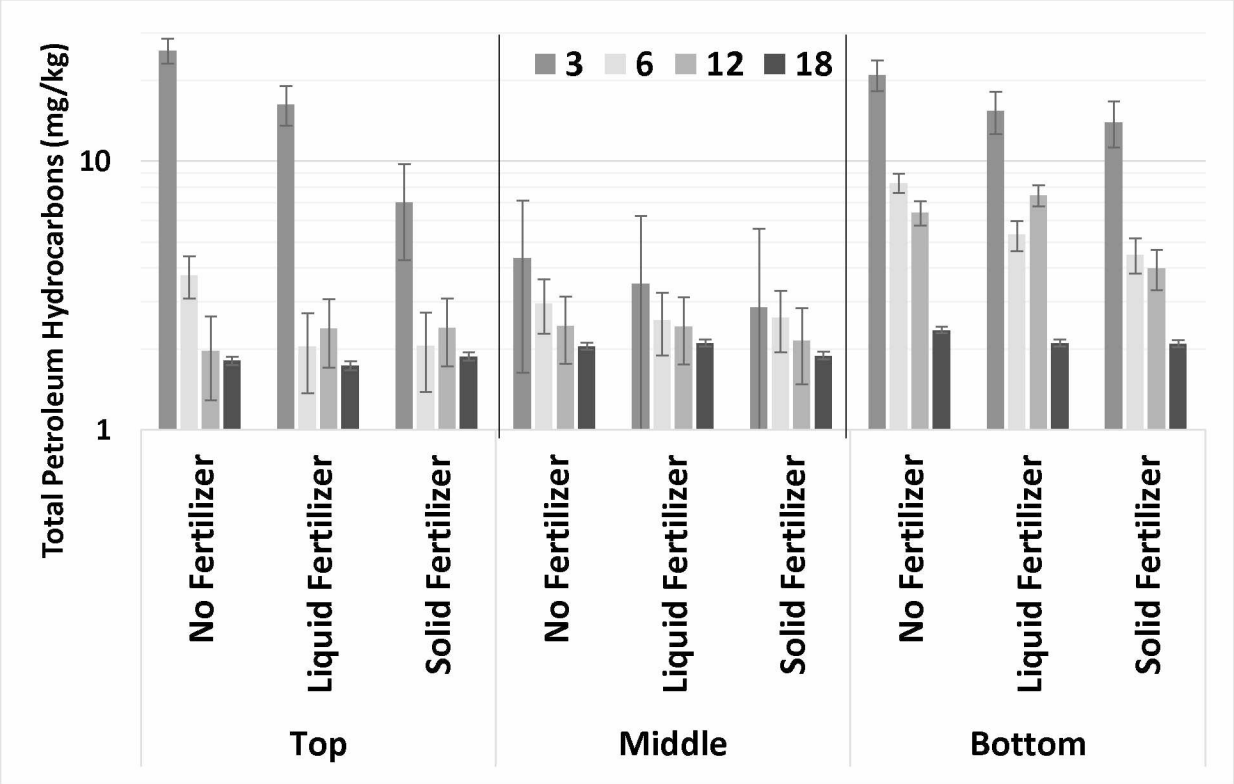

Figure 17: TPH concentration at different depths after 3-18 days in pebble sediment at 3°C. Error bars represent standard percentage error of 5% for the duplicate columns

4.2.2 Carbon Dioxide Release

Figure 18 and 19 show the amount of CO_2 that was released (average of duplicate columns) over 3, 6, 12, and 18 days for 20°C and 3°C respectively. Respiration data at 20°C followed the general trend that was seen in the sandy gravel sediment. Compared to Figure 11 for sandy gravel, where for the first 6 days all conditions showed comparable results (i.e. no effect of fertilizer or crude oil), we see this trend at day 12 for the pebble sediment. Only on day 18, the effect of crude oil mineralization on overall CO_2 production becomes noticeable. One reason that this consistent release extends to day 12 could be lower microbial numbers present in the pebble sediment, such that the microbial population could sustained by the original carbon source for a greater amount of time, which means a longer lag time occurred till crude oil was utilized. The reason why fewer microbes might be present has to do with the structure of the sediment. Due to the greater porosity there is a larger amount of air space within the sediment, and a smaller surface area of the sediment grains. Microbes in general favor lower porosity sediments, where they can be in contact with a greater amount of resources. If large gaps exist, the microbes additionally encounter the risk of being flushed out of the system.

Fertilization addition does appear to have a fairly significant effect on the release of CO_2 as time progresses, addition of liquid and solid fertilizer increases the amount of CO_2 being produced. It appears that the solid fertilizer was more effective than the liquid fertilizer. By day 6, the columns with fertilizer released almost 20 mg (solid) and 10 mg (liquid) more CO_2. At day 18 the fertilized columns released 40 mg (solid) and 20 mg (liquid) respectively more than the unfertilized column, showing that fertilizer in fact facilitates CO_2 production.

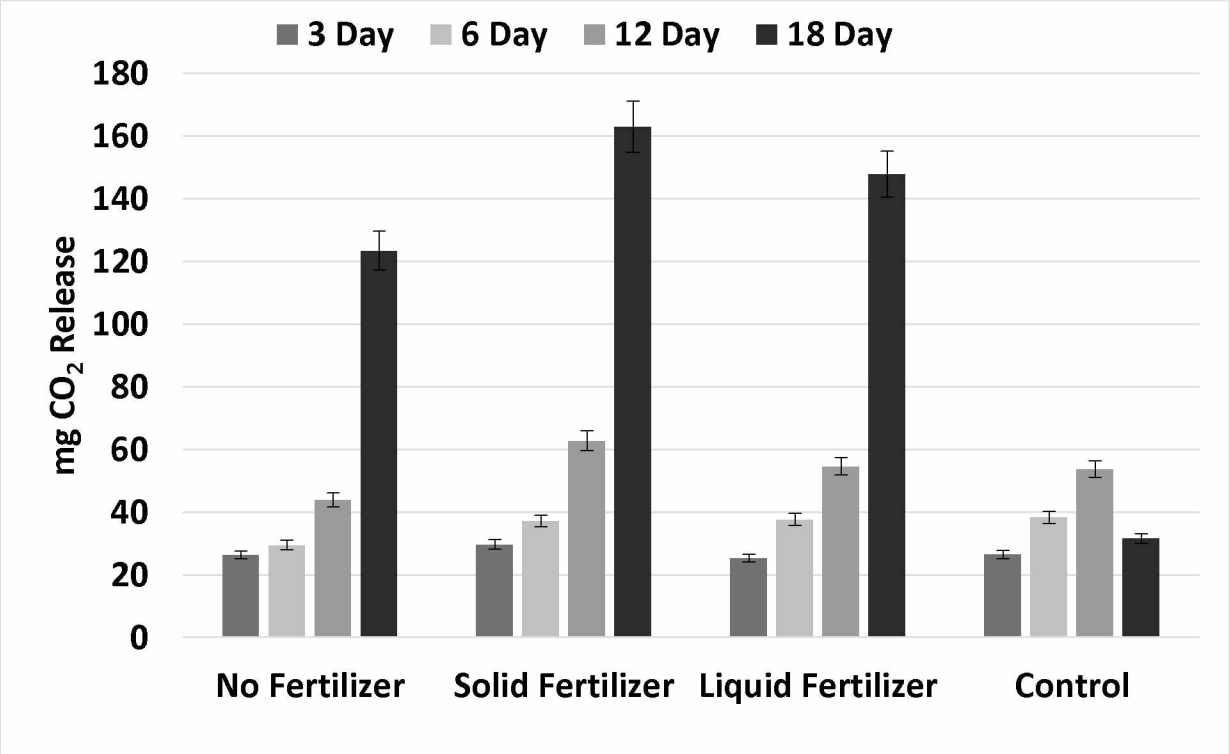

Figure 18: Cumulative CO_2 released from pebble sediment at 20 °C

Error bars represent standard percentage error of 5% for the duplicate columns

The CO_2 release from pebble sediment at 3°C shows a similar trend as at 20°C, with nearly identical CO_2 release for day 3, 6 and 12. On day 18 a much larger release of CO_2 was observed in the columns that contained crude oil. It is interesting that both the 20°C and 3°C studies have nearly identical releases for the first 12 days. However, once the original carbon content was depleted (around day 12) and the microbes moved on to the crude oil, we see that the release of CO_2 is much lower at 3°C than at 20°C. Apparently CO_2 production based on the original carbon source was independent of temperature. However as soon as crude oil mineralization commenced, temperature begins to show an effect.

The addition of fertilizer had some impact, with a roughly 20 mg more released in the columns with fertilizer. At day 6 and 12 both fertilizers a nearly identical small affect. By day 18, it appears

that unlike for the 20°C study, the liquid fertilizer had a slightly larger impact on the release of CO_2. Despite both fertilizers having a positive effect on the release of CO_2, it was only to a very small degree. Further experiments on mineralization rates past day 18 would be needed to determine if fertilizer causes a significant increase that would make it a cost effective option.

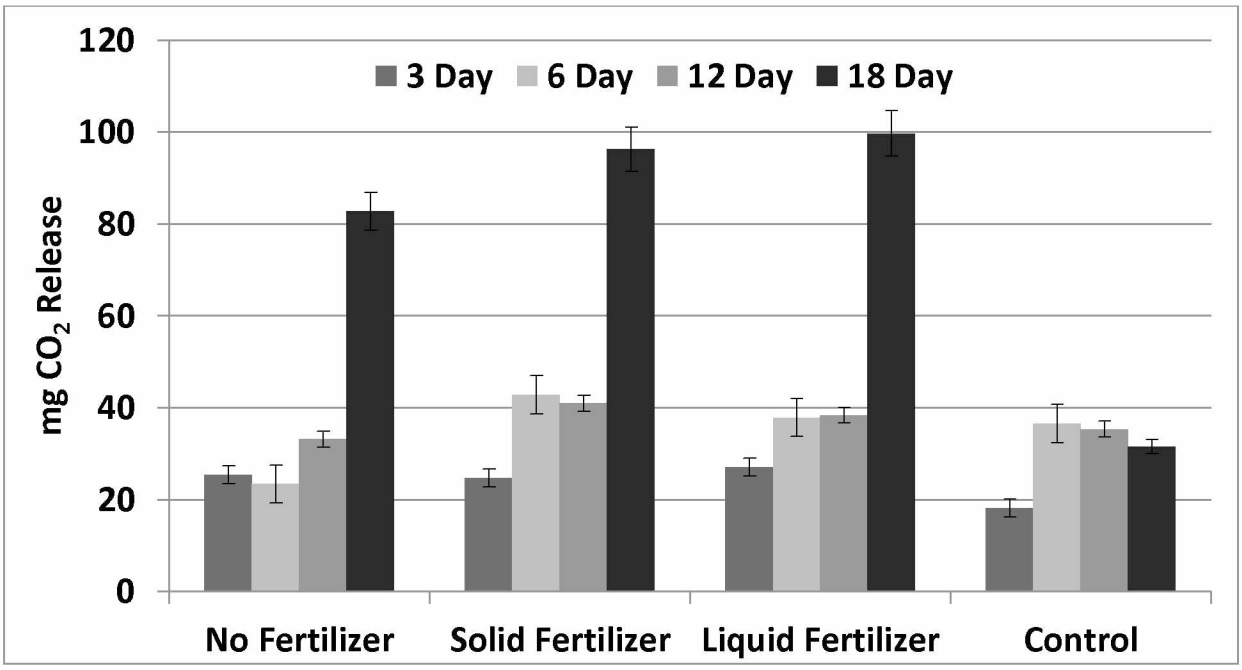

Figure 19: Cumulative CO_2 released from pebble sediment at 3°C

Error bars represent standard percentage error of 5% for the duplicate columns

4.2.3 Effect of Temperature and Fertilizer

Just as in the sandy gravel study, a higher loss of crude oil (i.e. lower TPH concentrations) was observed at 20°C compared to 3°C, although the trends are almost identical. The biggest difference between the two temperatures was observed at day 3. By day 6, however there was no real discernable difference between the two temperatures. It therefore seems that crude oil movement in pebble was not greatly affected by the change in viscosity as in the sandy gravel studies. This theory makes sense, as pebble sediments generally have a much larger pore size, which allows for water to drain quickly through the system.

In an environment with no fertilizer addition (Figure 20), the TPH concentrations in the sediment were generally slightly lower at 20°C than at 3°C. This means at the warmer temperature a slightly greater loss of crude oil from the system took place, especially during the first days. However there was no significant difference between TPH at 3°C and 20°C. In contrast to the sandy-gravel sediment, a much smaller difference between the two temperatures was observed, which again can be explained by the larger pore size which allows for the crude oil to penetrate more freely. It is therefore apparent that temperature had no significant impact on the movement of crude oil.

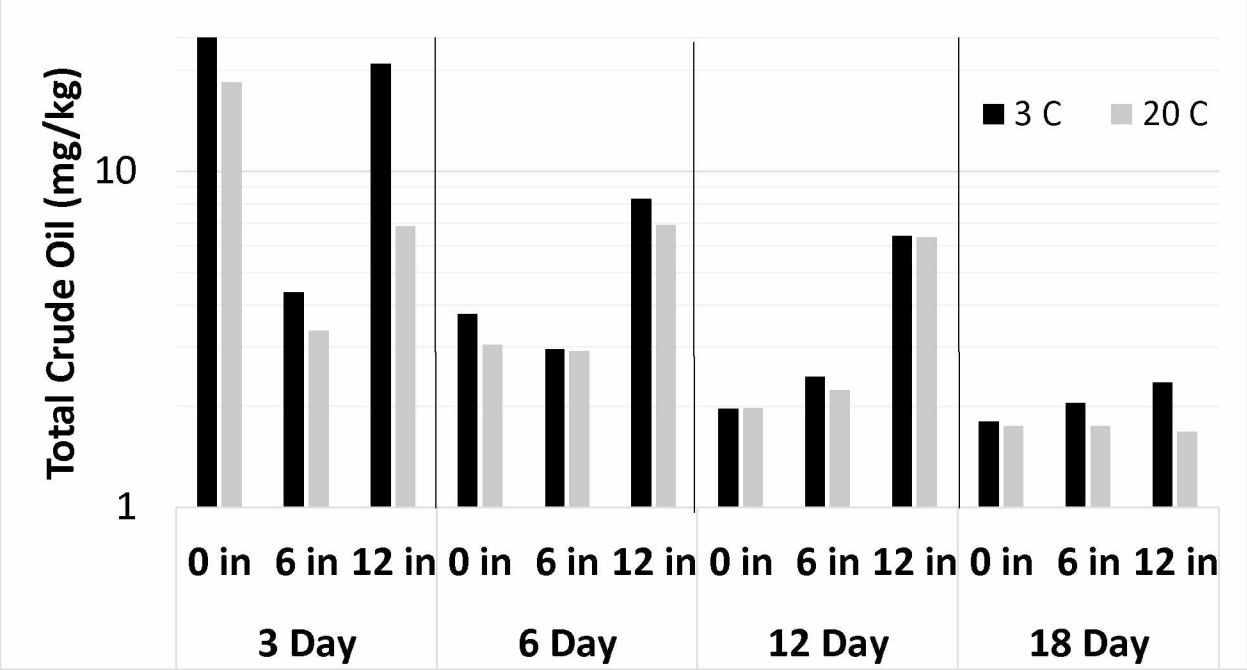

Figure 20: Temperature effect on crude oil movement with no fertilizer

Figure 21 shows the movement of oil in the presence of fertilizer. Just as with the previous figure, temperature does not appear to have a significant impact on the movement of crude oil.

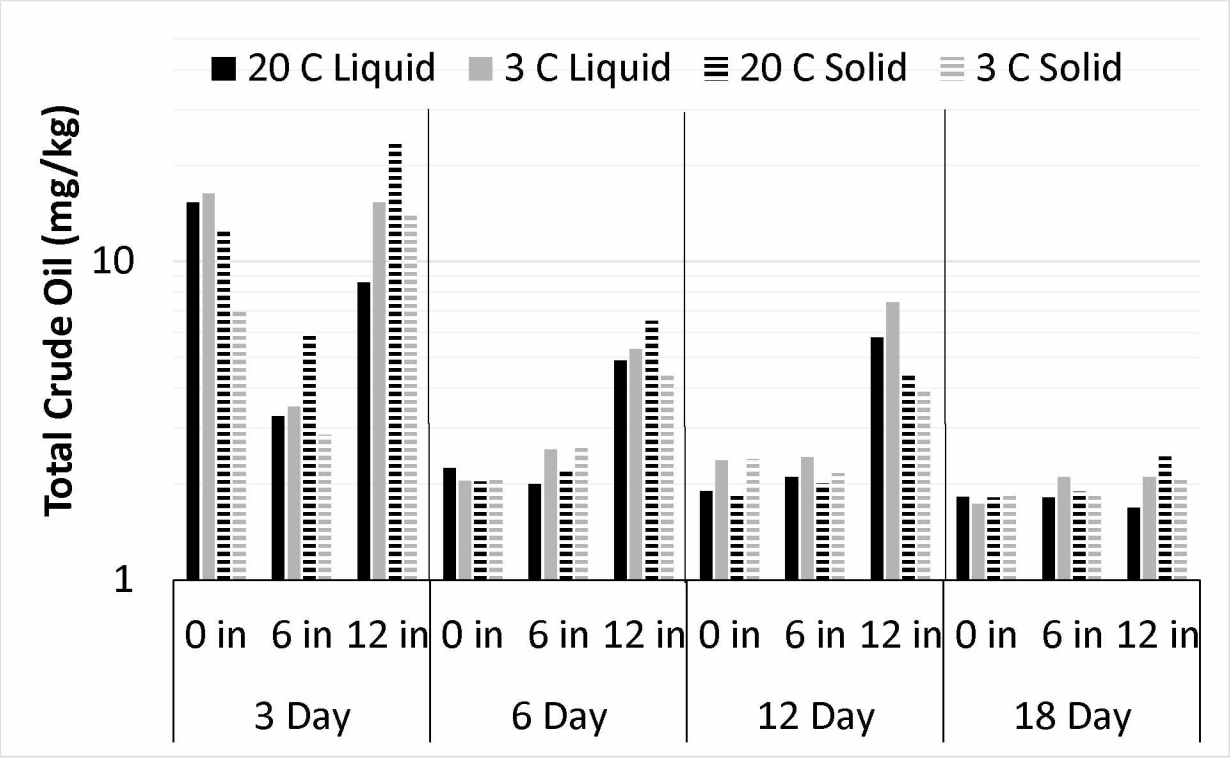

Figure 21: Temperature effect on crude oil movement with fertilizer

Figure 22 illustrates the release of CO_2 and its dependency on temperature. The graph shows CO_2 production for solid fertilizer (light lines) and liquid fertilizer (dark lines) as function of time. For the first six days the release of CO_2 is nearly identical for all temperatures and fertilizers. At day 12, we begin to see a significantly higher release at 20°C. Recall that it was concluded that at day 12 the organism have finally consumed the originally present natural carbon source and have moved on to the crude oil. This causes a significant increase in CO_2 release, especially at 20°C. At day 18, it is very clear that the warmer temperature showed a much greater release of CO_2 over time.

This trend makes sense, as stated before, microbes metabolize a higher amount of substrate at warmer temperatures and more readily degrade contaminants due to increased metabolic rates. It can be concluded that over the course of the first 12 days, as long as CO_2 production was due to

the natural carbon source, the temperature had no significant impact. However, once the microbes had to move to a new foreign substrate, the higher temperature lead to a faster mineralization rate.

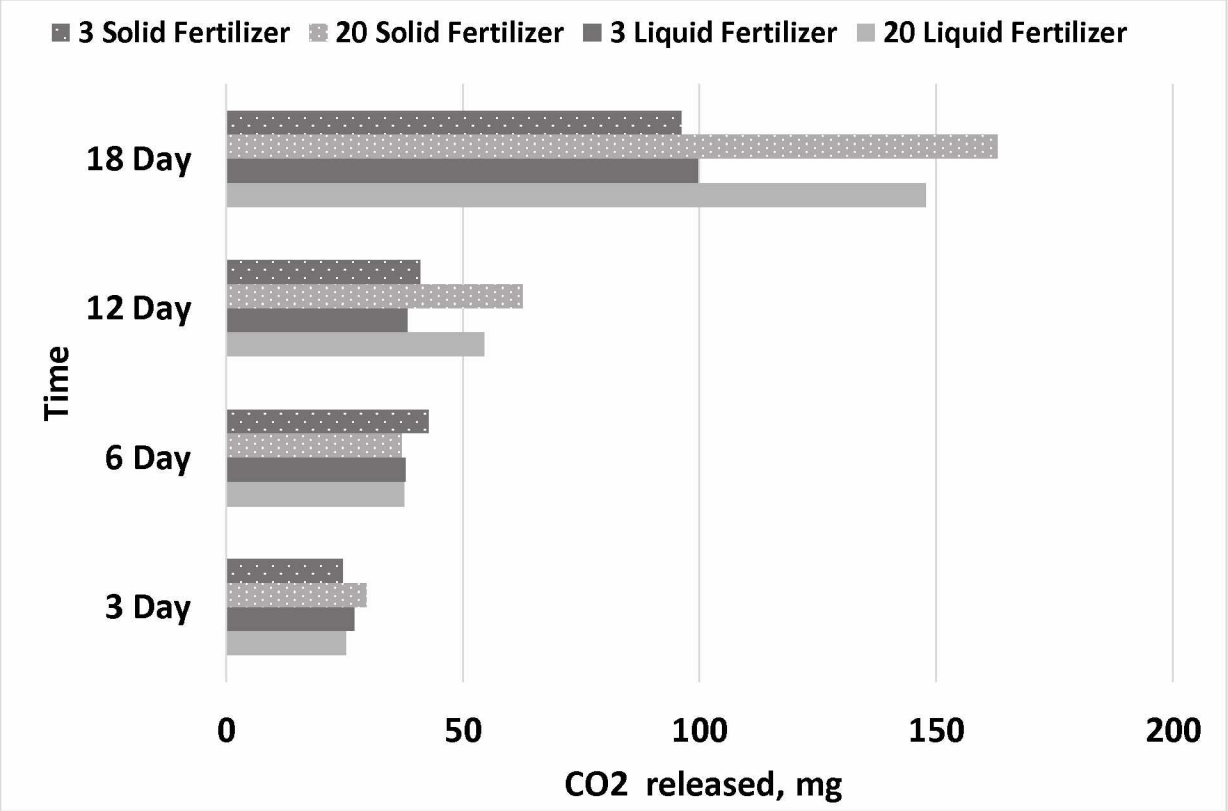

Figure 22: Temperature effect on release of CO_2 from pebble sediment with fertilizer

4.3 Comparison of Sandy Gravel and Pebble Sediment

4.3.1 Comparison of Sediment Types at 20°C

Figure 23 shows the distribution of crude oil in the column at 20°C, for both sediment types with no fertilizer addition. As already discussed above, the sandy-gravel sediment accumulated oil in the middle of the column, whereas pebble sediment showed a higher concentration initially at the top and later at the bottom of the column. In a natural environment, it appears that crude oil would remain in the sandy-gravel sediment for a much longer time frame. By day 6, the oil concentrations in pebble sediment have decreased significantly, where sandy gravel contained 29 mg or 10 times as much crude oil as the pebble sediment in the middle section. By day 12, the TPH values for sandy gravel become closer to pebble sediment in the top and bottom sections of the columns, but were still significantly higher in the middle.

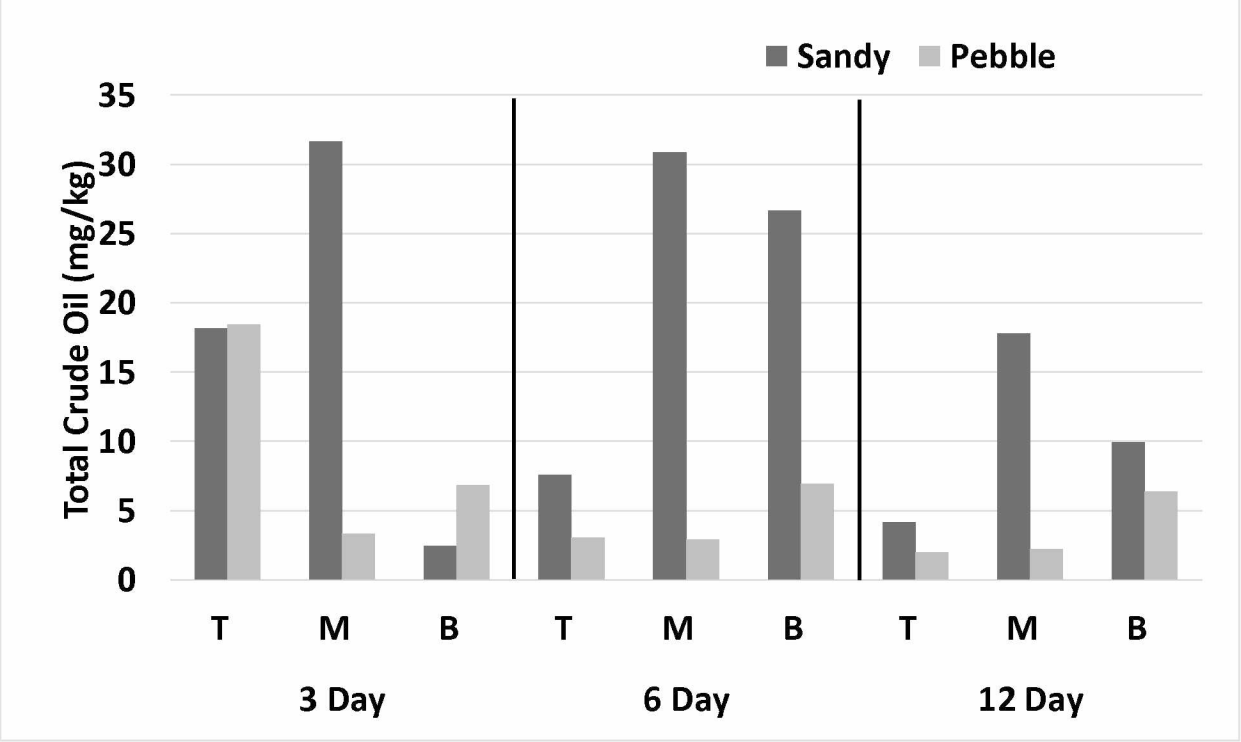

Figure 23: Impact of sediment type on crude oil movement at 20°C without fertilizer.

Figure 24 shows the movement of crude oil at 20°C in the presence of liquid fertilizer. The same general trend as described above is seen. However it should be noted that the initial concentration on day 3 at the top is significantly different. The TPH concentration in the sandy gravel was surprisingly low, maybe due to a measurement error.

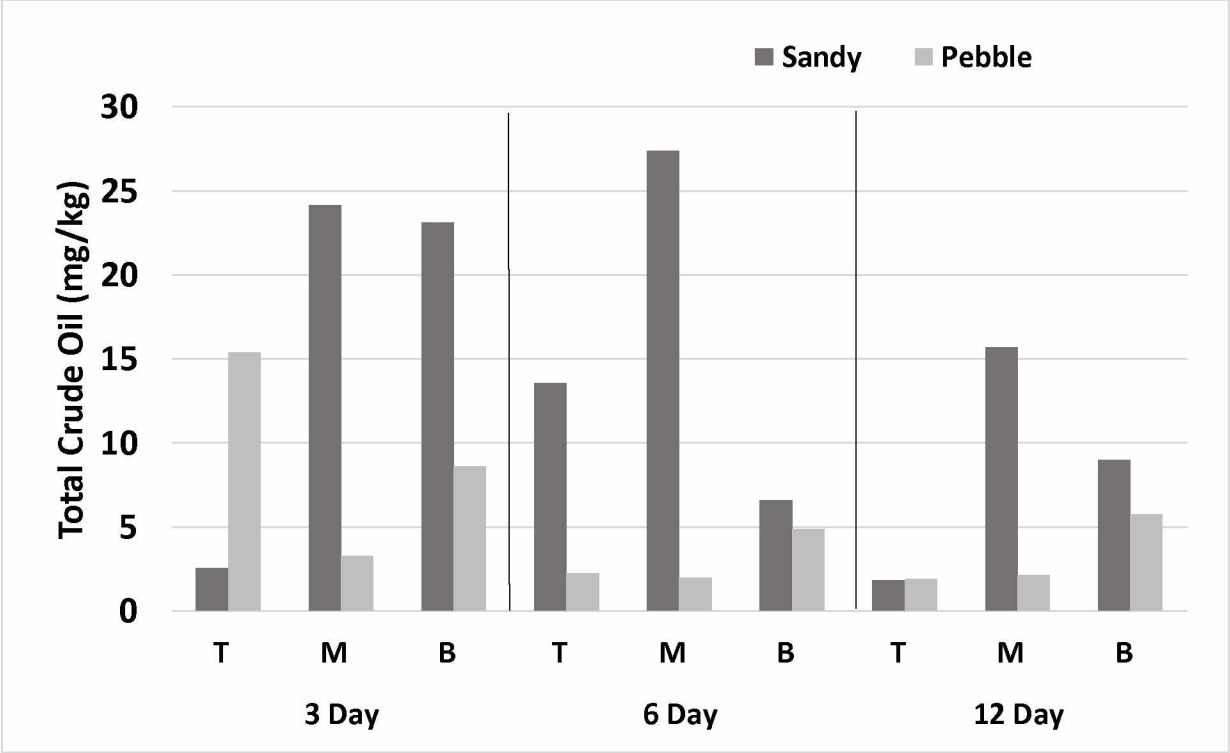

Figure 24: Impact of sediment type on crude oil movement at 20°C with liquid fertilizer.

Figure 25 shows how the release of CO_2 is impacted by the type of sediment. For the first 3 days, the pebble sediment is showing a higher release of CO_2, which is surprising. This could be related to the fact that at 20°C, a higher concentration of oil is found at the top layer during the first 3 days. However microbes should still be consuming their natural carbon source at this time and the crude oil should not be having a significant impact at this time, so the cause of the apparently higher respiration in pebble sediment is not clear. By day 6, a much higher CO_2 release occurred

for the sandy-gravel. One explanation for this could be that higher concentrations of microbes are often present in finer grained material (Lynch and Hobbie 1988). Additionally, the remaining concentration of crude oil in sandy gravel was higher (Figure 24), i.e. an increased amount of carbon source was available to the microbes.

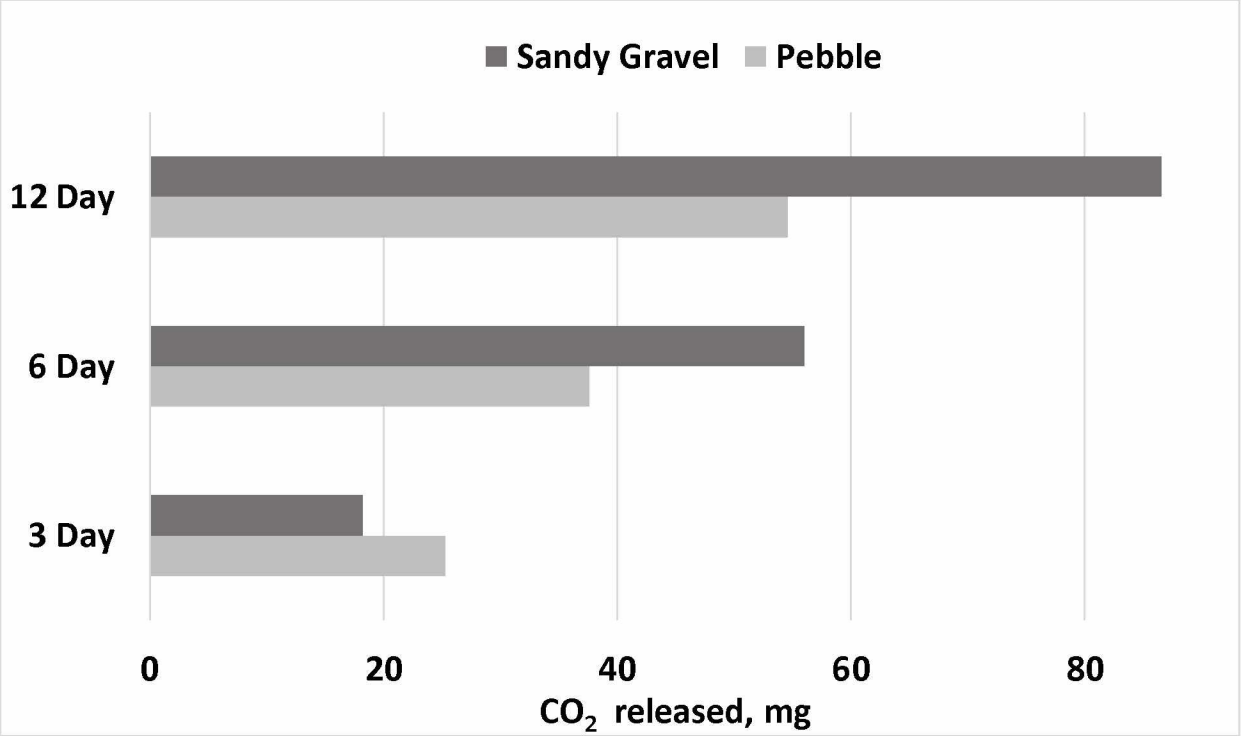

Figure 25: Impact of sediment type on CO_2 release at 20°C with liquid fertilizer.

4.3.2 Comparison of Sediment Types at 3°C

Figure 26 and 27 show the crude oil distribution at 3°C, without and with fertilizer addition, respectively. A similar trend as seen at 20°C is shown. There is higher crude oil concentration for pebble sediment over the first 3 days. However, the difference between the concentration levels decreased over time. From day 6 on, the crude oil concentration at the top and middle in sandy gravel was a multiple of that for pebble. At the bottom of the column, sandy gravel and pebble showed mostly similar concentrations, with a decreasing trend over time.

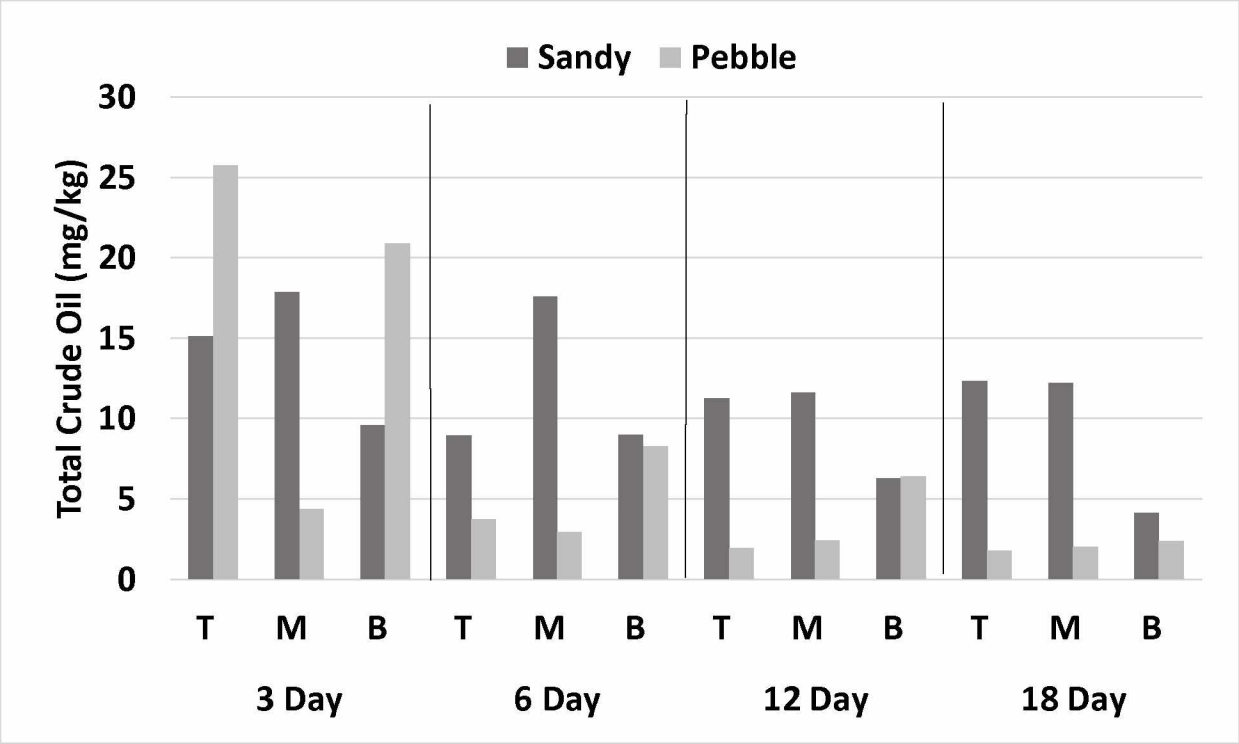

Figure 26: Impact of sediment type on crude oil movement at 3°C without fertilizer.

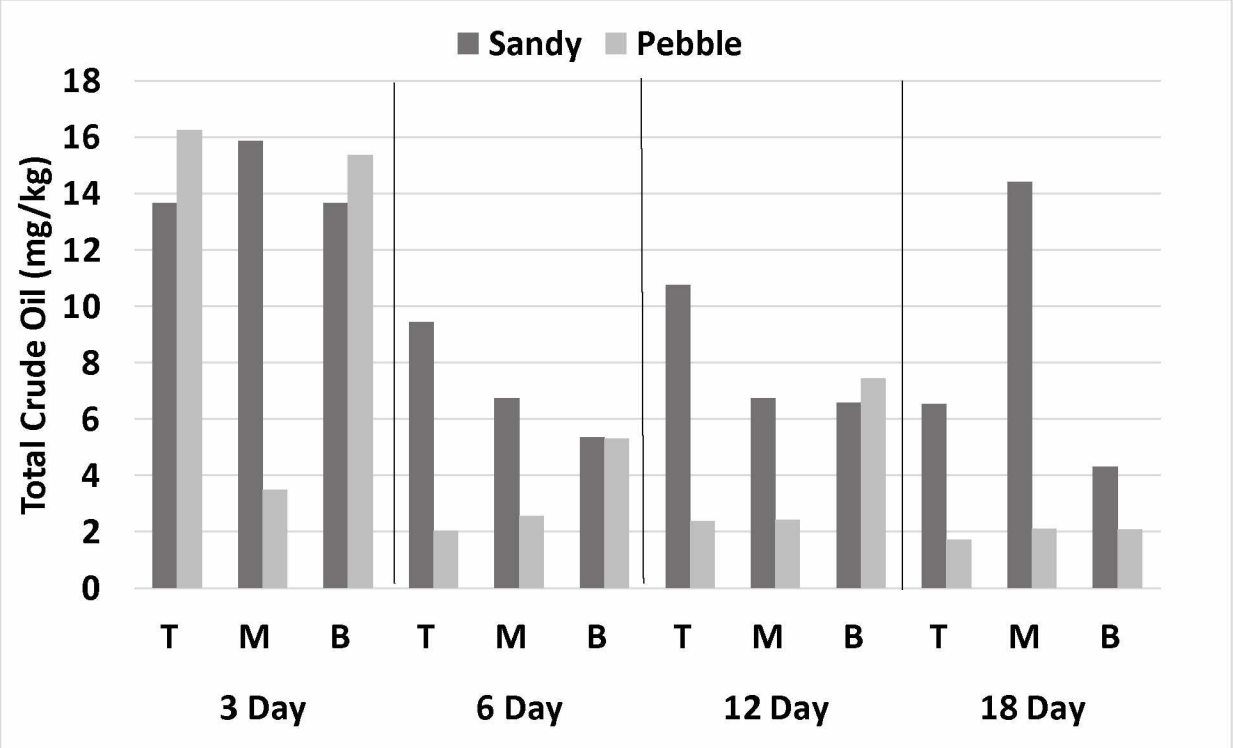

Figure 27: Impact of sediment type on crude oil movement at 3°C with liquid fertilizer.

Different results were observed with the additional of solid fertilizer. Unlike previous results, Figure 28 shows that after 3 days sandy-gravel had a much higher TPH concentration on the top than pebble. Concentrations in pebble were extremely low after the first 3 days in the top and middle sections of the column, with the highest crude oil concentrations at the bottom of the column, where it also reached background (2 mg) levels after 18 days. By day 6 similar trends as for the other fertilization regimes are shown, with lower concentrations in pebble sediment, and TPH values in sandy-gravel remaining relatively high in the top and middle sections.

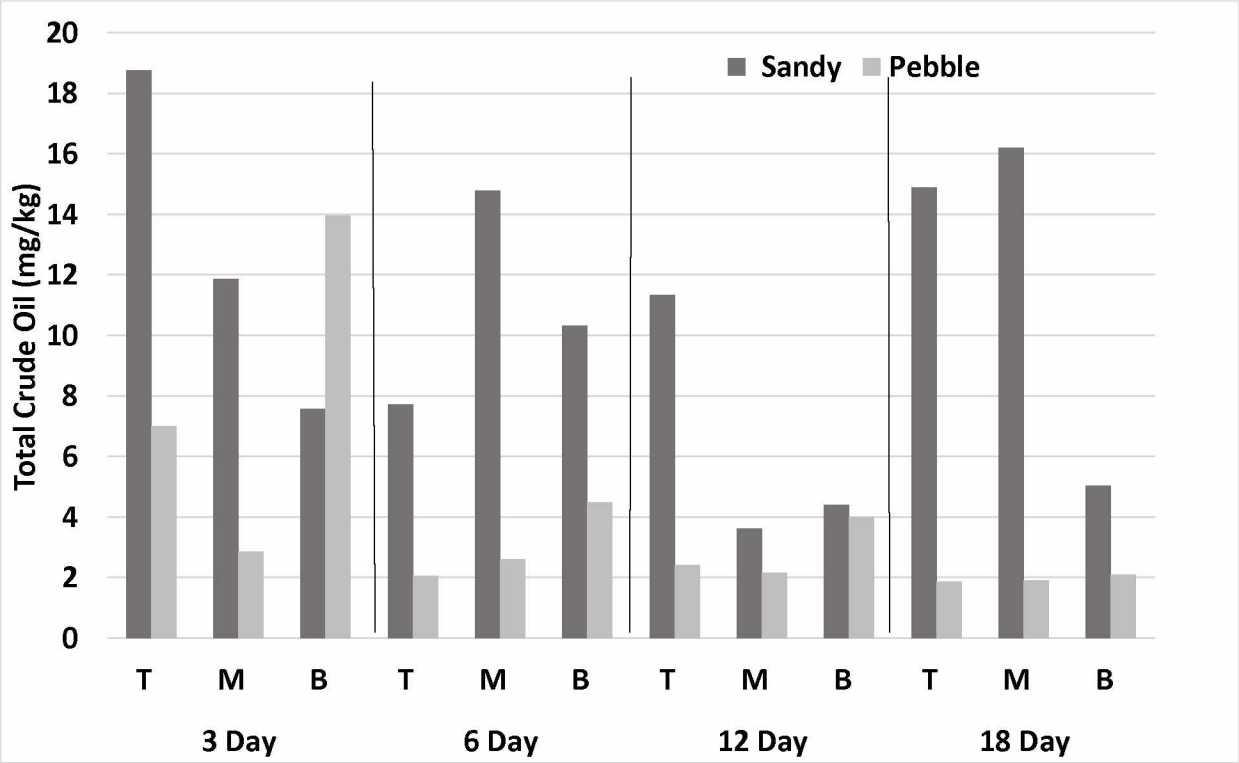

Figure 28: Impact of sediment type on crude oil movement at 3°C with solid fertilizer

Figure 29 shows the release of CO_2 in fertilized sediment at 3°C. Similar to the CO_2 release at 20°C, for the first 3 days, the pebble sediment is showing a higher release of CO_2. However unlike 20°C, at 3°C the pebble crude oil concentration was not significantly greater than the one in sandy-gravel, so a higher concentration of crude oil could not explain this higher release. By day 6, the two sediments have released nearly identical rates, over the next 12 days, we see a higher release of CO_2 in the sandy-gravel sediment. While it does appear that sandy-gravel has is a higher release of CO_2, but the difference is by less than 20 mg.

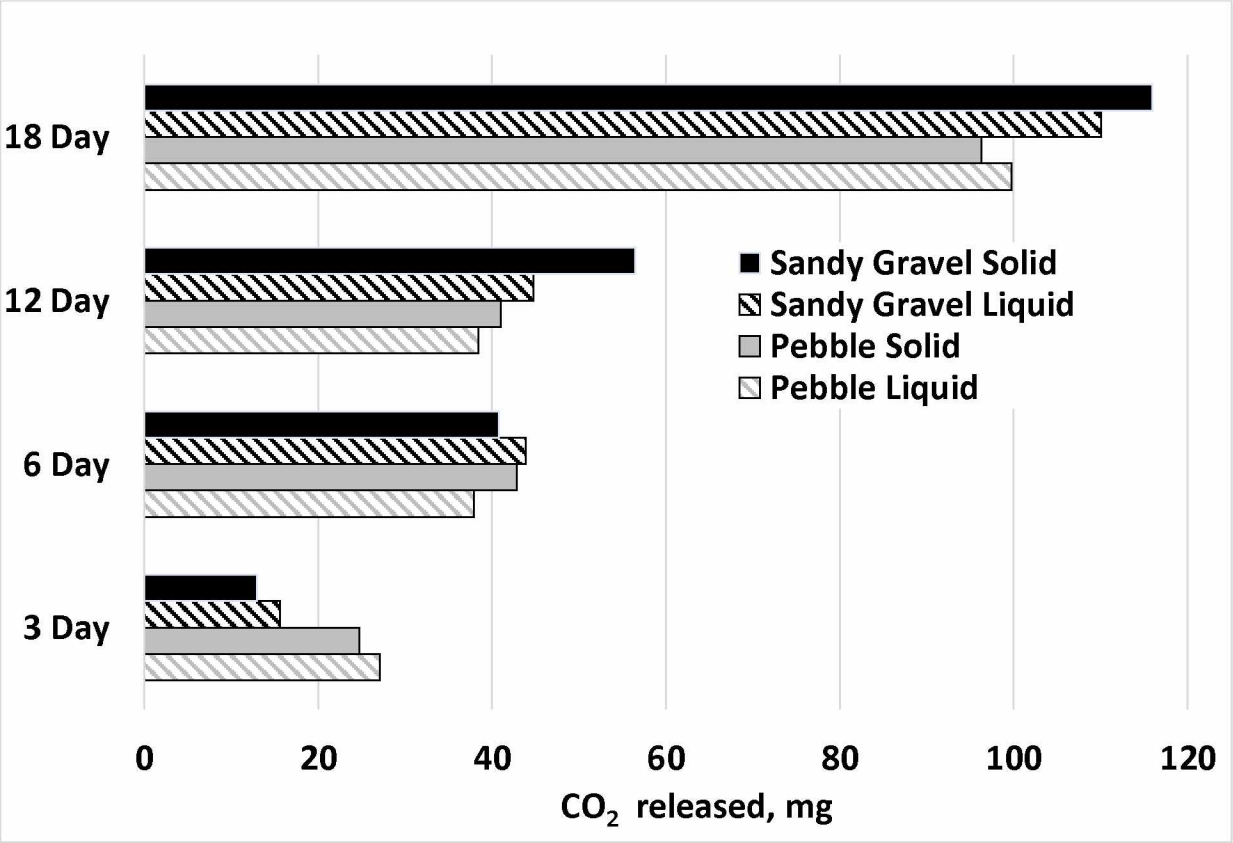

Figure 29: Impact of sediment type on CO_2 release at 3°C with fertilizer.

Chapter 5 Conclusions

5.1 Summary

The experiments have shown that the fate of crude oil was not strongly dependent on temperature, though respiration increased with temperature. The sediment type however had a significant impact on the fate of the crude oil. While fertilizer application can increase CO_2 production, this increase was not large enough to warrant nutrient addition. The following summary can be made for each sediment type and each temperature.

Sandy Gravel Sediment

- TPH persists 6 inches below surface for first 12 days
- Overall lower oil concentrations at 3 °C
- By day 12, TPH concentrations were roughly equal at both temperatures
- Higher crude oil retention than in pebble sediment (at both temperatures)
- Higher respiration than in pebble sediment, i.e. more biodegradation in sandy gravel
- Higher CO_2 release at 20°C

Pebble Sediment

- TPH persists at top and bottom of column
- Nearly identical TPH movement for both temperatures. By day 18, TPH concentrations are roughly equal at both temperatures
- Overall much lower TPH levels than in sandy gravel
- Higher CO_2 release at 20°C starting at day 12

- Liquid Fertilizer is most effective after day 12

20° C

- No large difference between sediment types
- Liquid fertilizer is more effective in sandy-gravel
- Solid Fertilizer is more effective in pebble

3° C

- Pebble sediment had initial higher CO_2 release
- Sandy gravel has significantly higher CO_2 release after day 3
- Neither sediment type nor fertilizer type have a significant impact on CO_2 release

The strong swash and backwash that affects the Arctic coastline, along with the beneficial nutrients of sea water, should facilitate crude oil removal from pebble sediments. Sandy-gravel sediments may require some additional effort, as pooling at 6 inches below the ground surface was encountered.

5.2 Future Research

While this experiment has provided some beneficial insight on how fertilizer and temperature can affect the fate of crude oil on an Arctic shoreline, further research would help to further explain the observed results and answer open questions.

Additional wave tank studies and the ability to collect and analyze the sediment would greatly help to show how the swash and backwash affect the crude oil movement.

Larger columns that extend at least 50 cm (the proposed depth that ESI 5 sediment will penetrate to) would be extremely useful.

Future studies should also find a way to measure the amount of nutrients washed out, and if other types of slow release fertilizer would be more effective.

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Appendix A Measured TPH in Controls

Measured TPH concentrations (mg/kg) in sediments for controls without crude oil are shown in the table below. Values were consistently at a very low level of 1.3-2.2 mg/kg.

Table 4: Measured TPH in Controls

		3 Day	6 Day	12 Day	18 Day
Sandy Gravel					
20°C	**Top**	**1.7**	**1.9**	**2.4**	**N/A**
	Middle	**1.4**	**1.7**	**2.6**	**N/A**
	Bottom	**1.9**	**1.7**	**2.9**	**N/A**
3°C	**Top**	**2.2**	**1.9**	**1.4**	**1.5**
	Middle	**2.0**	**1.5**	**1.5**	**1.3**
	Bottom	**2.1**	**1.6**	**1.4**	**1.3**
Pebble					
20°C	**Top**	**1.7**	**1.8**	**2.1**	**1.8**
	Middle	**1.8**	**1.7**	**1.8**	**2.0**
	Bottom	**1.8**	**1.8**	**1.8**	**2.0**
3°C	**Top**	**2.0**	**1.9**	**1.8**	**1.9**
	Middle	**2.0**	**1.9**	**2.0**	**1.9**
	Bottom	**1.9**	**1.7**	**1.8**	**1.8**

Appendix B Wave Tank Pictures

As described in section 3.4, the wave tank was set up by first adding the two sediment types separated by a Plexiglas division, forming a 30°slope (Figures 30, 31, 34a). Then artificial seawater was added (Figure 32, 34b). Finally waves were generated and crude oil was introduced (Figures 33, 34c)

Figure 30: Addition of pebble sediment

Figure 31: Addition of sand-gravel sediment

Figure 32: Waterline on sediments

Figure 33: Wave tank in action

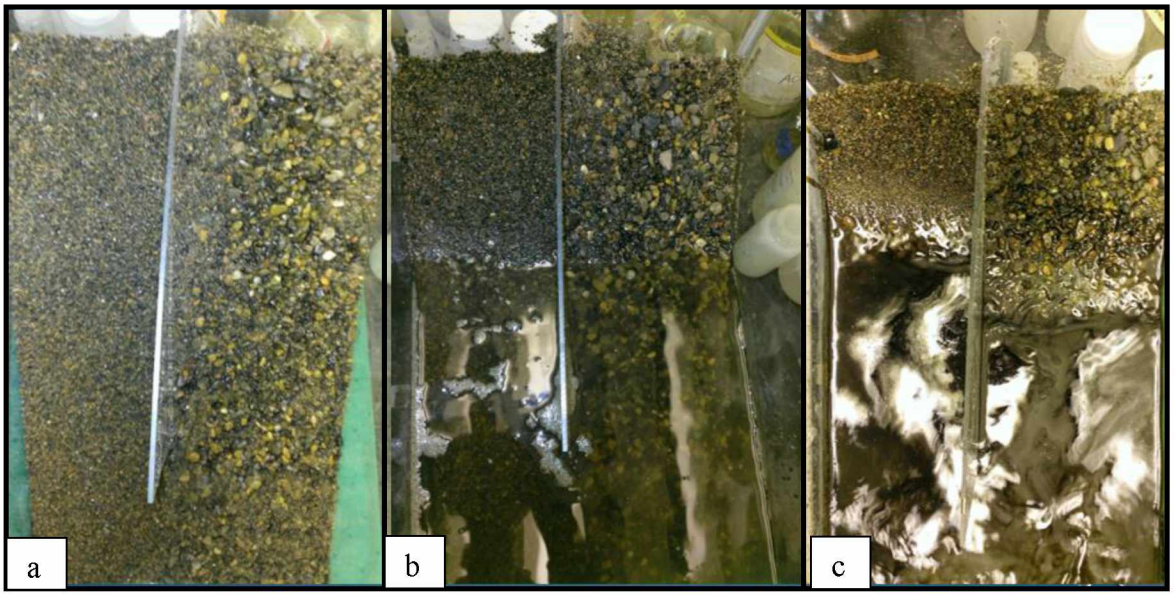

Figure 34: Sequence of steps in wave tank experiment, top view

a Sediment before water addition, b sediment with water, c sediment with water and crude oil